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| (54) Title: LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR MAKING AND ACIDIFYING THESE IONOMERS | | | | | |
| (57) Abstract | | | | | |
| <p>Ionomer compositions which have improved optical properties are disclosed. These compositions comprise ionomers which can be represented as the polymerization product of alpha-olefins having from two to eight carbon atoms, esters of alpha, beta-ethylenically-unsaturated carboxylic acids, metal salts of acrylic and methacrylic acid, and optional alpha, beta-ethylenically-unsaturated comonomers which impart some desired polymer property or properties, such as acidity and/or solvent resistivity. Also disclosed are methods of making these ionomer compositions in a reactive extruder and treating the compositions with acid to impart acidity to the compositions or to only the surface of the compositions.</p> | | | | | |

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1 LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC
2 ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR
3 MAKING AND ACIDIFYING THESE IONOMERS

4 BACKGROUND

5 This invention provides new polymeric ionomer compositions
6 which have low haze. Low haze makes the compositions
7 especially suited for use in clear packaging films, in
8 addition to the other applications in which ionomers are
9 utilized. This invention also provides a method for making
10 these new polymeric compositions and for modifying the
11 acidity of the compositions.

12 The compositions comprise ionomers which can be represented
13 as the polymerization product of alpha-olefins having from
14 two to eight carbon atoms, esters of alpha, beta-
15 ethylenically-unsaturated carboxylic acids, metal salts of
16 acrylic and methacrylic acid, and optional alpha, beta-
17 ethylenically-unsaturated comonomers which impart some
18 desired polymer property or properties, such as acidity
19 and/or solvent resistivity. These ionomer compositions can
20 easily be formed into films.

21 Ionomers which can be formed into films and methods of
22 making ionomers are known in the art. Although these
23 previously-known ionomers have similar chemical constituents
24 to the ionomer compositions of this invention, the known
25 ionomers have significantly different properties from the
26 compositions of this invention. In addition, the known
27 processes for making ionomers are also quite different from
28 the method of making compositions of the present invention.

29 Japanese patent number Sho 49-31556 to Iwami et al., dated
30 Aug. 22, 1974, discloses a process for making ionomers which
31 comprises saponifying copolymers of ethylene and alpha,

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1 beta-ethylenically-unsaturated carboxylate esters with a
2 basic metal compound in aliphatic alcohol or in an organic
3 solvent containing an aliphatic alcohol. The copolymer is
4 homogeneously or heterogeneously dispersed in the alcohol
5 solution. The saponified product can be further acidified
6 to provide a composition having acid groups. Although the
7 ionomers which have acid functionality are said to have low
8 haze, no haze values are provided for ionomers which have no
9 acid functionality.

10 Japanese patent number Sho 53-134591 to Harada et al., dated
11 Nov. 24, 1978, discloses a film made by the process of Sho
12 49-31556 which is said to be useful for stretch-wrap
13 applications. Their ionomer comprises a copolymer having
14 90-98 mole percent ethylene, 9.7 to 2.0 mole percent of an
15 alkyl ester of an unsaturated carboxylic acid, 0 to 2.5 mole
16 percent of unsaturated carboxylic acid, and 0.3 to 2.5 mole
17 percent of a metal salt of an unsaturated carboxylic acid.
18 It is stated that their film has very good mechanical,
19 thermal, and optical properties, but the film is limited to
20 having less than 9.7 mole percent ester because blocking
21 occurs between film layers. In addition, the copolymer is
22 limited to a maximum of 2.5 mole percent metal salt of an
23 unsaturated carboxylic acid due to the viscosity of the
24 copolymer being too high to allow processing of the
25 copolymer. All copolymers in the films of the examples
26 contain an unsaturated carboxylic acid component, which, the
27 patent states, are used to adjust the modulus of elasticity
28 and transparency of the film.

29 U.S. patent number 5,218,057, issued to V. Kurkov and
30 L. Theard on June 8, 1993 and which is incorporated by
31 reference in its entirety, teaches a process for saponifying
32 an ethylene alkyl acrylate copolymer which comprises adding
33 an aqueous solution of an inorganic alkali metal base to a

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1 molten ethylene-alkyl acrylate copolymer and mixing the
2 alkali metal base and copolymer at a temperature sufficient
3 for saponification to take place and at which the ethylene-
4 alkyl acrylate copolymer remains in a molten or fluid state.
5 Copolymers made by this process have lower tensile strength,
6 lower gloss, and much higher haze than the copolymers of the
7 present invention.

8 U.S. patent number 4,638,034 to McClain, dated Jan. 20, 1987
9 and which is incorporated by reference in its entirety,
10 claims a process for preparing an ethylene-acrylic acid
11 copolymer salt which comprises saponifying an ethylene-alkyl
12 acrylate copolymer in the molten state, in the absence of
13 solvent or water other than by-product alkanol, with alkali
14 metal hydroxide or alkaline earth metal hydroxide under non-
15 static mixing conditions so as to thereby form alkanol and
16 an alkali metal or alkaline earth metal salt of ethylene-
17 acrylic acid copolymer, and separately recovering the
18 alkanol and the salt.

19 U.S. patent number 3,970,626 to Hurst et al., dated July 20,
20 1976, discloses a copolymer of ethylene, alkyl acrylate or
21 methacrylate, and an alkali metal salt of acrylic or
22 methacrylic acid. Although this patent is mainly concerned
23 with forming copolymers which form stable aqueous emulsions,
24 the patent states that the copolymer can be extruded into
25 films of good flexibility. Copolymers in the examples are
26 formed using a batch autoclave. It is stated that about a
27 one-fold excess of sodium hydroxide over what is
28 theoretically required is used to convert the ester groups.

29 U.S. patent number 4,042,766 to Tatsukami et al., dated Aug.
30 16, 1977 and which is incorporated by reference in its
31 entirety, provides a method for preparing ionically cross-
32 linked copolymers comprising melt-blending a copolymer

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1 comprising 1) ethylene and 2) at least one alkyl acrylate or
2 methacrylate where the alkyl is selected from the group
3 consisting of isopropyl or tert-butyl, with 3) at least one
4 metal compound selected from the group consisting of
5 acetates, formates, and oxides of zinc, magnesium, calcium,
6 and sodium, and maintaining the molten blend at a
7 temperature of about 200 to 320°C. The patent states that
8 high mixing efficiency is desirable in the reaction
9 equipment to assure uniform dispersion of the metal compound
10 into the ester copolymer and to assure quick evaporation of
11 the low molecular-weight byproducts, such as by melt-
12 blending the components. Per the patent, adequate mixing
13 was provided by a 20 mm-diameter single-screw extruder
14 having a retention time of about one minute, as illustrated
15 in Example 1 of that patent.

16 U.S. patent number 3,789,035 to Iwami et al., dated Jan. 29,
17 1974 and which is incorporated by reference in its entirety,
18 discusses three methods for acidifying an ionomer of a
19 copolymer of ethylene and an ester of an alpha, beta-
20 ethylenically-unsaturated carboxylic acid. The ionomer is
21 made by saponifying a copolymer of ethylene and an ester of
22 an alpha, beta-ethylenically-unsaturated carboxylic acid
23 with a basic metal compound in a solvent containing an
24 alcohol. The patent states that the alcohol is used to
25 promote the reaction of the basic metal compound with the
26 copolymer. The ionomer is then acidified by either 1)
27 adding acid and replacing some of the basic metal with
28 hydrogen; 2) melt-blending a polymer having acid groups with
29 an ionomer; or 3) exchanging a non-alkali metal ion with the
30 alkali metal ion on the ionomer which has been dispersed in
31 a solvent.

32 U.S. patent number 3,264,272 to Rees, dated Aug. 2, 1966,
33 claims a composition comprising a random copolymer of an

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1 alpha-olefin having from two to ten carbon atoms, an alpha,
2 beta-ethylenically-unsaturated carboxylic acid having from
3 three to eight carbon atoms in which 10 to 90 percent of the
4 acid is neutralized with metal ions, and an optional third
5 mono-ethylenically unsaturated comonomer such as methyl
6 methacrylate or ethyl acrylate. This copolymer is acidic
7 due to the carboxylic acid groups present in the copolymer.
8 U.S. patent number 3,404,134 discloses the process for
9 making these compositions, which comprises reacting an
10 ethylene acrylic acid copolymer with a metal compound at a
11 pressure between 100 and 10,000 psi and a temperature above
12 the melt-point of the copolymer.

13 U.S. patent number 5,189,113 to Muehlenbernd et al., dated
14 Feb. 23, 1993, discloses a process for making ionically
15 cross-linked copolymers of ethylene and alpha, beta,
16 beta-ethylenically-unsaturated carboxylic acids or alpha, beta-
17 ethylenically-unsaturated comonomers donating carboxyl
18 groups, such as anhydrides. This process requires reacting
19 the copolymer with a solid metal compound in a mixing zone
20 of a twin-screw extruder and subsequently pumping in water.
21 The advantages for this process are said to be that no
22 discoloration of the ionomer occurs because no corrosion of
23 the twin-screw extruder occurs, and no specks of unreacted
24 solid metal compound are found in the ionomer film.

25 U.S. patent number 5,003,001 to Hasenbein et al., dated Mar.
26 26, 1991, claims a process for making ionically cross-linked
27 copolymers of ethylene and alpha, beta-ethylenically-
28 unsaturated carboxylic acids or alpha, beta-ethylenically-
29 unsaturated comonomers donating carboxyl groups, such as
30 anhydrides. This process reacts the copolymer with an
31 aqueous metal salt solution in a first reaction zone at a
32 temperature from 140 to 180°C to form ionomer and completely
33 devolatilizes the ionomer in a second, three-stage

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1 devolatilization zone at a temperature from 200 to 270°C.
2 This process is said to provide odor-free ionomer film which
3 is free of specks.

4 Although there has been much research in the area of
5 ionomers, what has been lacking in the prior art is
6 optically clear ionomers comprising copolymers of alpha
7 olefins having two to eight carbon atoms, esters of alpha,
8 beta-ethylenically-unsaturated carboxylic acids, and metal
9 salts of alpha, beta-ethylenically-unsaturated carboxylic
10 acids as well as methods of making those ionomers. This
11 invention provides such compositions and methods.

12 SUMMARY OF THE INVENTION

13 In one embodiment, the invention comprises a copolymer of
14 alpha-olefins having from two to eight carbon atoms, esters
15 of alpha, beta-ethylenically-unsaturated carboxylic acids
16 having from four to twenty-two carbon atoms, and metal salts
17 of acrylic or methacrylic acid, wherein this copolymer has a
18 haze of no more than ten percent as measured by ASTM method
19 D 1003.

20 In one preferred embodiment, the invention comprises a
21 copolymer of ethylene, methyl acrylate, and sodium salt of
22 acrylic acid, wherein the haze of the copolymer is no more
23 than five percent.

24 In another embodiment, the invention comprises a method of
25 making an ionomer composition. This method comprises
26 contacting a Group IA metal-containing solution with a
27 molten or fluid copolymer comprising alpha-olefins having
28 from two to eight carbon atoms and esters of alpha, beta-
29 ethylenically-unsaturated carboxylic acids having from four
30 to twenty two carbon atoms and having a melt index between
31 about 100 and about 2000 g/10 min., as measured by ASTM

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1 method D 1239 at 190°C using a 2.16 kg weight; and
2 intensively mixing the copolymer and Group IA metal-
3 containing solution at a temperature and to an extent which
4 provides an ionomer composition having no more than ten
5 percent haze.

6 In another embodiment, the invention comprises a method of
7 reducing the water solubility of an ionomer composition
8 formed into a shape such as strands, pellets, or film, which
9 method comprises contacting a surface of the shape with an
10 acid.

11 Among other factors, the present invention is based on our
12 finding that films of the composition as described herein
13 have very low haze, particularly when the films are made
14 after saponifying a copolymer as described above under
15 conditions which include intensive mixing, a greater extent
16 of saponification, and higher reaction temperatures. Film
17 haze is no more than ten percent, and many films have a haze
18 of no more than five or even two percent. Furthermore, in a
19 preferred embodiment, the composition has improved
20 properties such as improved tensile strength, hot tack
21 strength, and/or heat seal strength over ionomers of similar
22 composition.

23 In addition to the properties discussed above, many of the
24 compositions of this invention have no acidity, regardless
25 of the extent of saponification. These advantages and
26 others are further described below.

27 DESCRIPTION OF THE FIGURES

28 Figure 1 is a scanning electron micrograph of a freeze-
29 fractured cross-section of 3-mil thick film made from an
30 ionomer composition of this invention, taken at a
31 magnification factor of 8,000.

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1 Figure 2 is a scanning electron micrograph of a freeze-
2 fractured cross-section of 3-mil thick film of ionomer of
3 Comparative Example G. Figure 2 illustrates that spherical
4 and oblong ionic clusters or regions are present in the
5 ionomer. This micrograph was also produced at a
6 magnification factor of 8,000.

7 A JEOL JSM-820 scanning electron microscope was used to
8 generate the micrographs. The micrographs of Figures 1 and
9 2 show the fracture surface of films which were made by the
10 blown film process of the examples.

11 Figure 3 shows the hot-tack of ionomer of this invention
12 from Example 24 as a function of temperature. The ordinate
13 is temperature in °C, and the abscissa is hot-tack, measured
14 in Newtons/inch. Line 1 is 35% hydrolyzed ionomer, line 2
15 is 42% hydrolyzed ionomer, and line 3 is 50% hydrolyzed
16 ionomer.

17 Figure 4 shows the heat seal strength of the
18 ionomer/polyethylene film of Example 26 as a function of
19 temperature. The ordinate is temperature in °F and the
20 abscissa is the heat seal strength in lb/inch.

21 DETAILED DESCRIPTION OF THE INVENTION

22 A) Compositions

23 Compositions of this invention can be represented as the
24 copolymerization product which contains the following
25 comonomers:

26 (a) alpha-olefins having from 2 to 8 carbon atoms,
27 (b) esters of alpha,beta-ethylenically-unsaturated
28 carboxylic acids,

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- 1 (c) metal salts of acrylic or methacrylic acid, and
- 2 (d) optionally, other alpha, beta-ethylenically-unsaturated
3 comonomers which impart desirable polymer properties.

4 These compositions have no more than ten percent haze,
5 preferably no more than seven percent haze, and more
6 preferably, no more than five percent haze. The most
7 preferred compositions have no more than two percent haze.
8 Additionally, these compositions have very good hot tack
9 strength, heat seal strength, and mechanical properties such
10 as tensile strength. Acid functionality can also be
11 introduced into these ionomers.

12 Examples of compositions of this invention include ethylene-
13 methyl acrylate-sodium acrylate ionomer, ethylene-methyl
14 methacrylate-sodium methacrylate ionomer, ethylene-ethyl
15 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl
16 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl
17 methacrylate-sodium methacrylate ionomer, ethylene-methyl
18 acrylate-lithium acrylate ionomer, ethylene-methyl acrylate-
19 potassium acrylate ionomer, ethylene-methyl acrylate-
20 cobalt(II) or (III) acrylate ionomer, ethylene-methyl
21 acrylate-zinc acrylate ionomer, ethylene-methyl acrylate-
22 titanium(II), (III), or (IV) acrylate ionomer, ethylene-
23 methyl acrylate-magnesium acrylate ionomer, ethylene-methyl
24 acrylate-iron(II) or (III) acrylate ionomer, ethylene-methyl
25 acrylate-nickel(II) or (III) acrylate ionomer, ethylene-
26 methyl acrylate-copper(I) or (II) acrylate ionomer,
27 ethylene-methyl acrylate-acrylic acid-sodium acrylate
28 ionomer, ethylene-methyl methacrylate-methacrylic acid-
29 sodium methacrylate ionomer, ethylene-methyl acrylate-sodium
30 acrylate ionomer grafted with maleic anhydride, ethylene-
31 methyl acrylate-maleic anhydride-sodium acrylate ionomer,

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1 and acrylic acid-grafted-(ethylene-methyl acrylate-sodium
2 acrylate) ionomer.

3 Monomer (a) comprises alpha-olefins having from 2 to 8
4 carbon atoms. Preferably, monomer (a) comprises alpha-
5 olefins having from 2 to 3 carbon atoms, and more
6 preferably, monomer (a) consists essentially of ethylene.

7 Monomer (b) comprises esters of alpha, beta-ethylenically-
8 unsaturated carboxylic acids having from 4 to 22 carbon
9 atoms. Preferably, monomer (b) has from 4 to 13 carbon
10 atoms, and more preferably has from 4 to 8 carbon atoms.
11 Examples of monomer (b) include methyl acrylate, methyl
12 methacrylate, ethyl acrylate, ethyl methacrylate, butyl
13 acrylate, and butyl methacrylate. Methyl acrylate is the
14 preferred monomer (b).

15 Monomer (c) is a metal salt of acrylic or methacrylic acid.
16 The metal ion is selected from Group IA, Group IIA, and
17 transition metal ions. The metal ions may also be aluminum,
18 gallium, germanium, and tin. Other examples include
19 lithium, sodium, potassium, rubidium, cesium, calcium,
20 magnesium, zinc, titanium, iron, cobalt, nickel, and copper.
21 Preferably, the metal ion is a Group IA or Group IIA metal
22 ion, and more preferably, the metal ion is a Group IA metal
23 ion. Most preferred is sodium. Monomer (c) is about 25 to
24 99 mole percent of the total amount of (b) and (c) present
25 in a composition. Preferably, monomer (c) is about 35 to
26 80, and more preferably, is about 40 to 60, mole percent of
27 the total amount of (b) and (c) present in a composition.

28 Typically, a composition of this invention contains from
29 about 1 to 20 mole percent of monomers (b) and (c) in total.
30 Preferably, a composition contains about 3.5 to 12.5 mole
31 percent, and more preferably, about 5.5 to 10 mole percent

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1 of monomers (b) and (c). Most preferred is a composition.
2 containing about 7.5 to 10 mole percent of monomers (b) and
3 (c).

4 Monomer (d) is an alpha, beta-ethylenically-unsaturated
5 comonomer which imparts certain desired polymer properties.
6 The amount and type of monomer (d) is determined by the
7 particular properties that are desired in the final
8 composition. For example, monomer (d) may be acrylic or
9 methacrylic acid which is present in an amount that provides
10 the desired acid functionality to the composition. Other
11 examples of monomer (d) include maleic anhydride and maleic
12 acids to impart acidity, acrylonitrile to impart solvent
13 resistance, and styrene to increase the rigidity of the
14 composition. Typically, the compositions contain 0 to 10
15 mole percent of monomer (d). Preferred compositions contain
16 0 to 5 mole percent of monomer (d).

17 Monomer (d) can also be added by grafting a group such as
18 acrylic acid or maleic anhydride to a composition of the
19 present invention or to one of the composition's precursors.
20 As a result, compositions can comprise grafted (ethylene,
21 (meth)acrylate, metal salt of (meth)acrylic acid)
22 copolymers. Maleic anhydride-grafted (ethylene, methyl
23 acrylate, sodium acrylate) copolymer is one such
24 composition.

25 The ionomer compositions of this invention have a number of
26 surprising features which distinguish them from other
27 ionomers having similar chemical constituents. The ionomers
28 of this invention are quite clear. Haze is typically no
29 more than 5 percent. Also, in one preferred embodiment, the
30 60° gloss is typically at least 100, and in many instances,
31 is at least 120. In another preferred embodiment, tensile
32 strength of the composition is improved over ionomers of

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1 similar composition by 100-300 percent. Hot-tack strength
2 and heat seal strength can also be improved over ionomers of
3 similar composition. Combinations of these improved
4 features are present in some preferred compositions of this
5 invention.

6 For example, the haze, gloss, and tensile strength of
7 ionomer of this invention are substantially different from
8 the haze, gloss, and tensile strength of ionomer made by the
9 process of U.S. Pat. № 5,218,057. Ethylene-methyl acrylate
10 copolymer having about 20 weight percent (about 7.5 mole
11 percent) methyl acrylate and having about 65% of the methyl
12 acrylate saponified with aqueous sodium hydroxide according
13 to the process of U.S. Pat. № 5,218,057 had a haze of 15%
14 and 60° gloss of 66. Tensile strength of an ethylene-methyl
15 acrylate copolymer having 20 weight percent methyl acrylate
16 which had about 60% of the methyl acrylate groups saponified
17 with aqueous sodium hydroxide according to the process of
18 U.S. Pat. № 5,218,057 was 1582 psi in the machine direction.
19 A composition of the present invention made by saponifying
20 an ethylene-methyl acrylate copolymer having about 20 weight
21 percent methyl acrylate with aqueous sodium hydroxide to
22 convert about 65% of the methyl acrylate groups had a haze
23 of 2%, gloss of 133, and tensile strength in the machine
24 direction of 4010 psi.

25 The ionomers of this invention also can be formed into very
26 thin film. When blowing film, the blow-up ratio can be as
27 high as 2:1 to about 2.5:1. Typically, a film of ionomer of
28 this invention can have a thickness of less than about 1
29 mil. Film having a thickness of about 0.5 mil has been
30 made, and film having a thickness of about 0.2 - 0.3 mil can
31 be made on conventional processing equipment.

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1 The morphology of prior art ionomers can also differ
2 substantially from the morphology of ionomers of this
3 invention. The morphology of prior art ionomers can also
4 differ substantially from the morphology of ionomers of this
5 invention. Prior-art ionomers can contain highly localized
6 and large clusters of ionic material dispersed throughout
7 the ionomer. Scanning-electron micrographs have shown that
8 these clusters can range in size from about 0.05 micron to
9 greater than 1 micron in size.

10 Figure 2 is a scanning-electron micrograph for the ionomer
11 of Comparative Example G. This ionomer consists essentially
12 of ethylene, 5.7 mole percent methyl acrylate, and 1.8 mole
13 percent of the sodium salt of acrylic acid. The spherical
14 or oblong ionic clusters evident in this micrograph range in
15 size from about 0.1 micron to about 0.5 micron. The
16 clusters were determined to be ionic by energy-dispersive
17 X-ray spectroscopy, which showed a higher sodium content
18 within the clusters when compared to the surrounding
19 continuous phase.

20 Figure 1 is a scanning-electron micrograph for ionomer
21 composition of this invention, which consists essentially of
22 ethylene, 3.7 mole percent methyl acrylate, and 3.7 mole
23 percent of the sodium salt of acrylic acid. This ionomer
24 composition is substantially free of ionic clusters of the
25 size seen in Figure 2, since essentially no ionic clusters
26 are observed in this micrograph. An ionomer composition
27 which is substantially free of ionic clusters contains
28 essentially no ionic clusters about 0.05 micron in size or
29 larger when a freeze-fractured cross-section of 3-mil thick
30 blown film which is made by the method of Example 1 is
31 viewed with a scanning electron microscope at a
32 magnification factor of 8,000. An ionomer composition which
33 is substantially free of ionic clusters will also have a

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1 haze of no more than ten percent. The ionomer composition
2 of Figure 1 corresponds to the composition of Example 12,
3 which had a haze of 3%. The large flecks of debris in
4 Figure 1 are believed to be foreign matter. The flecks are
5 not regions having high sodium content.

6 Additives well-known in the art may be included in the
7 ionomer, such as anti-block and slip additives and anti-
8 oxidants. Preferably, the composition of this invention
9 also contains a polymeric acid having a molecular weight of
10 less than about 10,000, such as ethylene acrylic acid.
11 Ionomer compositions containing these low molecular weight
12 acids are disclosed in copending U.S. Ser. No. 08/188,848,
13 filed Jan. 31, 1994, which is incorporated by reference in
14 its entirety herein.

15 B) Method for making the compositions

16 One method for making compositions of this invention
17 comprises saponifying a copolymer having ester groups with a
18 Group IA metal-containing solution. To obtain the clear
19 ionomer compositions of this invention, it is important to
20 provide intensive mixing of the copolymer and the Group IA
21 metal-containing solution and to have a temperature and/or
22 extent of saponification high enough that a substantially
23 uniform saponification of the copolymer occurs. This method
24 minimizes the production of localized ionomer regions or
25 domains, which appear as the spherical and oblong ionic
26 clusters of Figure 2. This method also permits a greater
27 extent of saponification of the copolymer without obtaining
28 a saponified product that has so high of a viscosity that it
29 cannot be formed into a film on conventional equipment.

30 Intensive mixing of the reaction components results from
31 selection of reactants with the appropriate physical and
32 chemical characteristics and selection of the proper

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1 processing conditions. Particular processing conditions are
2 discussed below for a reactive extruder. However, the
3 general principles disclosed therein apply to processes
4 which are equivalent to saponifying a copolymer with a
5 Group IA metal-containing solution in a reactive extruder.

6 (1) Reactants

7 (a) Copolymer to be saponified

8 The copolymers which are saponified comprise copolymers of
9 ethylene, esters of alpha, beta-ethylenically-unsaturated
10 carboxylic acids, and optional alpha, beta-ethylenically-
11 unsaturated comonomers which impart desirable polymer
12 properties. Typically, these copolymers contain from about
13 1 to 20 mole percent of esters of alpha, beta-ethylenically-
14 unsaturated carboxylic acids in total. Preferably, the
15 copolymers contain about 2 to 20 mole percent, more
16 preferably 3.5 to 12.5 mole percent, and even more
17 preferably, about 5.5 to 12.5 mole percent of esters of
18 alpha, beta-ethylenically-unsaturated carboxylic acids in
19 total. Most preferred are those copolymers containing about
20 6.5 to 10 mole percent of esters of alpha, beta-
21 ethylenically-unsaturated carboxylic acids. The preferred
22 esters are alkyl acrylates. Preferably, the alkyl group
23 contains from one to eight carbon atoms, and more preferably
24 contains from one to four carbon atoms. Methyl is a
25 preferred alkyl group.

26 Examples of the copolymers which are saponified include
27 ethylene-methyl acrylate copolymer, ethylene-methyl
28 methacrylate copolymer, ethylene-ethyl acrylate copolymer,
29 ethylene-propylene-methyl acrylate copolymer, ethylene-
30 propylene-methyl methacrylate copolymer, ethylene-methyl
31 acrylate-acrylic acid copolymer, ethylene-methyl
32 methacrylate-methacrylic acid copolymer, maleic anhydride-
33 grafted-ethylene-methyl acrylate copolymer, ethylene-methyl

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1 acrylate-maleic anhydride copolymer, acrylic acid-grafted-
2 ethylene-methyl acrylate copolymer, and ethylene-methyl
3 acrylate-butyl acrylate copolymer. Preferably, the
4 copolymers are ethylene-methyl acrylate copolymer, ethylene-
5 methyl methacrylate copolymer, ethylene-ethyl acrylate
6 copolymer, maleic anhydride-grafted-ethylene-methyl acrylate
7 copolymer, and ethylene-methyl acrylate-butyl acrylate
8 copolymer. Most preferred is ethylene-methyl acrylate
9 copolymer.

10 The melt index of copolymers to be saponified should be
11 between about 100 and 2000, preferably between about 200 and
12 800, and more preferably between about 300 and 600 grams/10
13 minutes. Copolymers having higher melt-index values are
14 preferred when it is desired to have a saponified
15 composition with a higher melt index. One process for
16 making these copolymers comprises polymerizing ethylene,
17 alkyl acrylate and/or alkyl methacrylate, and the optional
18 comonomer in autoclaves using free-radical initiation
19 catalysts. This process is described in U.S. Patent
20 No. 3,350,372, which is incorporated by reference in its
21 entirety. The copolymers of the examples were made by this
22 method, unless specified otherwise. In one preferred
23 embodiment, the ethylene-alkyl acrylate copolymer is made by
24 the process described in copending U.S. Ser. No. 07/947,870,
25 filed Sep. 21, 1992 (published as WO 93/06137), which is
26 incorporated by reference in its entirety herein. Copolymer
27 made by this process has a substantially higher melt-point
28 temperature than the copolymer made by the process of U.S.
29 Patent No. 3,350,372. The ionomer of this invention has
30 high melt point temperature and high clarity when made with
31 this copolymer. Another process for producing copolymers
32 useful in making the ionomer compositions of this invention
33 comprises free-radical polymerization of ethylene and alkyl
34 acrylate and/or alkyl methacrylate as described above,

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1 followed by reactive extrusion with a compound such as
2 acrylic acid or maleic anhydride. Alternatively, grafting
3 may be performed after saponification. A particularly
4 preferred copolymer is ethylene-methyl acrylate copolymer
5 having between about 5.5 and 12.5 mole percent methyl
6 acrylate and having a melt index of about 400 g/10 min.,
7 available from Chevron Chemical Company as EMAC® copolymer.

8 (b) Group IA metal-containing solution

9 The Group IA metal-containing solution comprises a Group IA
10 metal in a solvent, which solvent does not prevent
11 saponification of an ester by the Group IA metal. The
12 solvent is preferably one which evaporates readily under
13 devolatilization conditions typically encountered in
14 reactive extruders. Solvents can be organic or inorganic,
15 and common solvents include water, alcohols, and
16 polyethylene glycols, with water being preferred.

17 The Group IA metal-containing solution has at least one
18 Group IA metal present. Preferably, the solution comprises
19 an aqueous solution of a Group IA metal oxide and/or
20 hydroxide, such as oxides and hydroxides of lithium, sodium,
21 potassium, rubidium, and/or cesium. Preferably, the
22 Group IA metal-containing solution comprises aqueous sodium
23 hydroxide or aqueous potassium hydroxide.

24 It is important that the overall concentration of metals in
25 the Group IA metal-containing solution is low enough that
26 the solution is capable of being mixed uniformly and
27 intensively with melted copolymer in a reaction section of a
28 reactive extruder. However, it is preferred to have only
29 that amount of solvent present that is necessary to provide
30 this capability. Normally, a sufficient quantity of solvent
31 is present when the Group IA metal-containing solution
32 contains little or no excess solvent beyond that required to

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1 solubilize essentially all of the Group IA metal and other
2 metals present. Thus, for example, 50% aqueous caustic
3 solution is preferred over 35% aqueous caustic solution.

4 The Group IA metal-containing solution may optionally
5 contain other metal oxides, hydroxides, and/or salts which
6 supply cations for monomer (c). The metal ions can be
7 alkaline earth or transition-element metals. Specific
8 examples of these metals include calcium, magnesium, zinc,
9 titanium, cobalt, nickel, and copper. Typical anions
10 include hydroxide, halide, acetate, propionate, decanoate,
11 and stearate ions, with acetate ions being preferred anions.
12 The hydroxide form is also preferred.

13 Instead of being present in the Group IA metal-containing
14 solution, metal ions (including Group IA metal ions) may
15 optionally be incorporated into the ionomer composition of
16 this invention by other methods. One method is to first
17 saponify a copolymer by the method of this invention, then
18 totally or partially replace the ion of this ionomer
19 composition with other metal ions under ion-exchange
20 conditions, or to react the ionomer composition with an
21 aqueous metal hydroxide. For example, an ion-exchange
22 solution comprising an aqueous solution of zinc oxide or
23 zinc acetate may be mixed with a sodium ionomer composition
24 of this invention in a section of a reactive extruder to
25 replace at least a portion of the sodium ions with zinc
26 ions.

27 Examples of metal ions which may be exchanged include the
28 alkaline metals, alkaline earth metals such as magnesium,
29 transition metals such as titanium, cobalt, copper, and
30 zinc, and other metal ions such as aluminum, gallium,
31 germanium, and tin.

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1 The anion of a salt used to ion-exchange the ionomer is
2 preferably one which is easily washed out of the ionomer and
3 separated from it during filtration. Alternatively, the
4 anion is preferably one which forms an easily-evolved
5 compound or one which evolves or whose products of
6 decomposition evolve at devolatilization conditions in a
7 reactive extruder. Typical anions include chloride,
8 acetate, propionate, decanoate, and stearate ions. Acetate
9 ions are preferred.

10 (2) Reactive Extruder

11 A reactive extruder which is useful in producing
12 compositions of this invention comprises an extruder having
13 a copolymer feed section, one or more reaction sections, a
14 subsequent devolatilization section, and an extrusion
15 section. Typically, these sections are separately jacketed
16 to allow for heating or cooling within each section. These
17 sections can also be vented with one or more vent ports per
18 section to allow the escape of volatile components, such as
19 the solvent for the Group IA metal solution and byproducts
20 of the saponification reaction, such as alcohols.
21 Generally, the reactive extruder will also have optional
22 means for introducing reactants into any reaction sections
23 as well as means for mixing components in the reaction
24 section(s) and means for conveying the components through
25 the extruder. Typically, the means for mixing and conveying
26 components to be reacted are screws.

27 Reactive extruders can have a single screw or multiple
28 screws. Each screw typically has a central shaft with a
29 key-way or spline upon which mixing elements are secured.
30 The reactive extruder may have either co-rotating or
31 counter-rotating screws.

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1 Typically, copolymer to be reacted is fed to the screw
2 through a loss-in-weight feeder, and the solid copolymer is
3 melted in a feed section of the reactive extruder. In some
4 embodiments, all reactants (i.e. copolymer and Group IA
5 metal-containing solution) can be fed to the reactive
6 extruder through a feed section. In a preferred embodiment,
7 copolymer is introduced into the reactive extruder in a feed
8 section, and the Group IA metal-containing solution is fed
9 to one or more reaction sections. A devolatilization
10 section is a convenient means for removing any solvent and
11 byproducts of the saponification reaction from the
12 saponified composition. Equivalent or additional means for
13 removing volatile components can be used, however, such as
14 drying the ionomer composition under reduced pressure in a
15 falling-film evaporator.

16 One reactive extruder which was particularly effective in
17 producing compositions of this invention is a Werner-
18 Pfleiderer co-rotating and intermeshing twin-screw extruder.
19 The reactive extruder had a feed section, a reaction
20 section, a devolatilization section, and a pressurization or
21 pumping section which pushed the product through an
22 extrusion die. The devolatilization section had a first
23 portion which was vented to a condenser maintained at
24 atmospheric pressure, and a second portion of the
25 devolatilization section was vented with sufficient vacuum
26 and capacity to remove essentially all of the volatile
27 components from compositions prior to conveying and
28 extruding them.

29 Typically, copolymer pellets are introduced into a feed
30 section of a reactive extruder, where the pellets are heated
31 and worked by the screw to form molten or fluid copolymer.
32 The screw elements also convey the molten copolymer from
33 this feed section to a first reaction section, where the

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1 molten copolymer and Group IA metal-containing solution are
2 mixed intensively.

3 Intensive mixing can be supplied by incorporating one or
4 more reverse-flow elements along with neutral or reverse-
5 flow kneading blocks on the screw in a reaction zone. The
6 copolymer to be saponified and the Group IA metal-containing
7 solution should be mixed as uniformly and as quickly as
8 possible to provide a fairly uniform reaction of metal-
9 containing solution with the molten copolymer. Mixing
10 should be of sufficient intensity that saponification of
11 only localized areas is prevented.

This intensive mixing is of greater intensity than that required in the prior-art processes of U.S. Pat. № 4,638,034 and U.S. Pat. № 4,042,766. For example, a Werner-Pfleiderer Model ZSK-40 twin-screw reactive extruder had the configuration of screw elements detailed in Table 1 column A. This screw design provided intensive mixing of the Group IA metal-containing solution with copolymer in the reaction section through a combination of left-handed elements and neutral kneading blocks. It is believed that the left-handed elements in the reaction section provide momentary retardation of polymer flow in addition to a shear zone due to impeded and/or reversed flow of the reaction mass, while the neutral kneading blocks imparted intensive mixing and promoted additional shear. Most of the compositions of this invention were produced at a screw speed of about 400 to 550 rpm. High screw speeds help to assure intensive mixing.

TABLE 1

| ELEMENT NUMBER | COLUMN A | COLUMN B | COLUMN C |
|-------------------|----------|----------|----------|
| | | | |

SUBSTITUTE SHEET (RULE 26)

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| | | | | |
|----|----|------------------------|---------------------|--------------|
| 1 | 1 | 40/20 ¹ | PKR/10 ² | PKR/10 |
| 2 | 2 | 60/60 | 20/10 | 20/10 |
| 3 | 3 | 60/60 | 42/42 | 42/42 |
| 4 | 4 | 40/40 | 42/42 | 42/42 |
| 5 | 5 | 40/40 | 42/42 | 28/28 |
| 6 | 6 | 40/40 | 28/28 | 28/28 |
| 7 | 7 | 40/20 | 28/28 | 28/28 |
| 8 | 8 | 40/40 | 20/20 | 20/20 |
| 9 | 9 | 25/25 | 20/20 | 20/20 |
| 10 | 10 | KB45/5/40 ³ | 20/20 | 20/20 |
| 11 | 11 | KB45/5/40 | KB45/5/28 | 20/10 |
| 12 | 12 | 25/25 | KB45/5/28 | KB45/5/28 |
| 13 | 13 | 25/25 | 20/20 | KB45/5/28 |
| 14 | 14 | 25/25 | 20/20 | 20/20 |
| 15 | 15 | 40/20 LH ⁴ | KB90/5/28 | 20/20 |
| 16 | 16 | 25/25 | 20/10 LH | 20/10 LH |
| 17 | 17 | KB90/5/40 | 20/20 | 20/10 LH |
| 18 | 18 | 25/25 | 20/20 | 20/10 LH |
| 19 | 19 | KB90/5/40 | KB45/5/28 | 20/20 |
| 20 | 20 | 25/25 | 20/10 | 20/20 |
| 21 | 21 | 40/20 LH | 20/20 | KB45/5/28 |
| 22 | 22 | 25/25 | 20/20 | 20/10 |
| 23 | 23 | KB90/5/40 | KB90/5/28 | 20/20 |
| 24 | 24 | 25/25 | 20/20 | 20/20 |
| 25 | 25 | KB90/5/40 | KB45/5/14 LH | KB90/5/28 |
| 26 | 26 | 25/25 | KB45/5/14 LH | 20/20 |
| 27 | 27 | 40/20 LH | 20/20 | KB45/5/14 LH |
| 28 | 28 | KB45/5/20 LH | 20/20 | KB45/5/14 LH |
| 29 | 29 | 25/25 | KB90/5/28 | 20/20 |
| 30 | 30 | 25/25 | 20/20 | 20/20 |
| 31 | 31 | 25/25 | 20/20 | KB90/5/28 |
| 32 | 32 | 25/25 | 20/20 | 20/20 |
| 33 | 33 | 25/25 | 20/20 | 20/20 |
| 34 | 34 | 40/40 | 20/20 | 20/20 |

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| | | | | |
|----|----|--------------|-----------|-----------|
| 1 | 35 | 40/40 | KB90/5/28 | 20/20 |
| 2 | 36 | 40/40 | 20/20 | KB90/5/28 |
| 3 | 37 | KB45/5/20 LH | 20/20 | 20/20 |
| 4 | 38 | 40/40 | 20/20 | 20/20 |
| 5 | 39 | 40/40 | 20/20 | 20/20 |
| 6 | 40 | 40/40 | 20/20 | 20/20 |
| 7 | 41 | 40/40 | 20/20 | KB90/5/28 |
| 8 | 42 | 25/25 | 20/20 | 20/20 |
| 9 | 43 | 25/25 | 20/20 | 20/20 |
| 10 | 44 | 25/25 | KB90/5/28 | 20/10 |
| 11 | 45 | 25/25 | 20/20 | 20/20 |
| 12 | 46 | 25/25 | 20/20 | 20/20 |
| 13 | 47 | 25/25 | 20/10 LH | 20/20 |
| 14 | 48 | 25/25 | 20/10 LH | 20/20 |
| 15 | 49 | 25/25 | 20/20 | 20/20 |
| 16 | 50 | 25/25 | 20/20 | 20/20 |
| 17 | 51 | 25/25 | 20/20 | 20/20 |
| 18 | 52 | 25/25 | 20/20 | 20/20 |
| 19 | 53 | 25/25 | 42/42 | 20/20 |
| 20 | 54 | 25/25 | 42/42 | 20/20 |
| 21 | 55 | 25/25 | 42/42 | 42/42 |
| 22 | 56 | | 20/20 | 42/42 |
| 23 | 57 | | 20/20 | 42/42 |
| 24 | 58 | | 20/20 | 28/28 |
| 25 | 59 | | 20/20 | 20/20 |
| 26 | 60 | | 20/20 | 20/20 |
| 27 | 61 | | | 20/20 |

28 NOTES:

29 1. All elements were right-handed elements unless
 30 designated otherwise. The first number is the pitch,
 31 given in distance (mm) traveled in one revolution. The
 32 second number is the length of the element (mm).

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- 1 2. The PKR element is a wedge-shaped adapter which
- 2 provides a taper from the 1/2 inch shaft to the first
- 3 element of the screw.
- 4 3. KB indicates a kneading block. The first number is the
- 5 angle formed by the paddles on the kneading block when
- 6 compared to the line through the screw shaft, in
- 7 degrees. The second number is how many paddles are on
- 8 one element. The third number is the length of the
- 9 element (mm).
- 10 4. "LH" indicates a left-handed element.

11 (3) Reaction conditions

12 Reaction temperature, feed-rate of reactants, and extent of

13 saponification are also important processing parameters when

14 making compositions of this invention.

15 (a) Reaction temperature

16 Compositions of this invention are typically produced where

17 the barrel temperature in the reaction section(s) of the

18 extruder is between about 200 and 350°C, although some clear

19 ionomers were prepared at a temperature between about 150

20 and 200°C. Any reaction temperatures discussed herein refer

21 to the barrel temperatures of the extruder. The actual

22 temperature of the melted polymer is believed to be lower

23 than the measured barrel temperature because of heat-

24 transfer limitations.

25 Preferably, the reaction temperature is between 225 and

26 350°C, and, more preferably, the temperature is between

27 about 275 and 350°C. The upper limit of the temperature

28 range is determined by the temperature at which the

29 copolymer or composition degrades. The lower limit of the

30 temperature range is the temperature at which 1) the

31 copolymer to be reacted is in a molten or fluid state;

32 2) essentially all of the Group IA metal in the Group IA

- 25 -

1 metal-containing solution is consumed by the saponification
2 reaction within the reaction section; and 3) the composition
3 being extruded remains visually clear. As a general rule,
4 higher reaction temperatures as specified in the more
5 preferable range above provide low-haze ionomers more
6 consistently than lower reaction temperatures.

(b) Feed rate of reactants

8 The Group IA metal-containing solution is fed in an amount
9 that is effective to achieve the desired extent of
10 saponification of the copolymer being fed to the reactive
11 extruder. Typically, essentially all of the Group IA metal
12 in solution reacts with the copolymer. The Group IA metal-
13 containing solution may be fed to a reaction section batch-
14 wise or continuously, or it may be fed intermittently so
15 that the solution is mixed intimately and rapidly with the
16 molten copolymer. A continuous feed is preferred. The
17 Group IA metal-containing solution may also be split between
18 multiple reaction sections and be fed continuously and/or
19 intermittently to any reaction section.

20 The copolymer to be saponified is fed to the reactive
21 extruder at a rate high enough that the molten polymer forms
22 a molten polymer seal between consecutive segments of a
23 reaction section and between a reaction section and a
24 devolatilization section. This seal can be formed by having
25 a reverse-flow screw element at the desired seal location.
26 The feed-rate should also be low enough that the reaction
27 mass comprising the copolymer to be saponified and the
28 Group IA metal-containing solution does not move through the
29 reaction section so quickly that the reaction mass is not
30 mixed intensively. The feed-rate should also be low enough
31 that the extruded polymer is visually clear, corresponding
32 to no more than ten percent haze.

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1 The copolymer to be saponified may be fed to the extruder
2 batch-wise, intermittently or continuously. A continuous
3 feed is preferred to provide a commercially-attractive
4 process which is easily and effectively controlled.

5 Typically, the average residence time for reactants in a
6 Werner & Pfleiderer ZSK-40 twin-screw extruder which has a
7 feed section, one reaction section, devolatilization
8 section, and pumping section is about 30 to about 40 seconds
9 at a continuous feed-rate of approximately 100 lb./hr. of
10 polymer to be saponified and at a screw speed of about 500
11 rpm. The average residence time in the reaction section of
12 this reactive extruder at these conditions is typically
13 about 5 to about 15 seconds.

14 When the feed-rate is too high to make a composition of this
15 invention, the screw torque will decrease, and the ionomer
16 will turn cloudy. Both of these conditions can be observed
17 almost immediately upon feeding too much copolymer to the
18 extruder. Visually, the extruded copolymer turns from clear
19 to cloudy, and when a strand of the cooled copolymer is
20 pulled in the direction in which it was extruded, the cloudy
21 copolymer turns whitish and opaque.

22 (c) % saponified

23 The extent of saponification is defined as the percent of
24 moles of esters of alpha, beta-ethylenically-unsaturated
25 carboxylic acids converted to metal salts of acrylic and
26 methacrylic acid. Compositions of this invention have been
27 produced where the extent of saponification of the ester
28 groups in the copolymer has been between about 25 and 99%.
29 Ionomer which has an extent of saponification below about
30 25% above are typically cloudy and have poorer gloss, melt
31 strength, and/or tensile strength than compositions of this
32 invention. A greater extent of saponification generally

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1 produces low-haze ionomers more consistently than a low
2 extent of saponification, particularly when the reaction
3 temperature is between about 150 and 225°C.

4 C) Acidification

5 Acidification of a polymer is a useful method for modifying
6 polymer properties. In one preferred embodiment, ionomers
7 of this invention have essentially no acidity. These
8 ionomers can be represented as copolymers comprising
9 comonomers of alpha-olefins, esters of alpha, beta-
10 ethylenically-unsaturated carboxylic acids, and metal salts
11 of alpha, beta-ethylenically-unsaturated carboxylic acids.
12 The properties of these non-acidic ionomers can be modified
13 by adding acid groups.

14 Also, some of the ionomers of this invention are highly
15 water-dispersible. This can be an advantage for
16 applications where repulpable compositions are desired, such
17 as repulpable paper coatings and adhesives. However, water
18 dispersibility is a problem where the ionomer composition is
19 cooled in a water-bath after saponification, which is a
20 common commercial method of cooling polymers. Much of the
21 ionomer to be cooled can end up dispersed in the cooling
22 water, turning the water a milky white color.

23 Other cooling means may be used for handling highly water-
24 dispersible ionomers, such as hot-face cutting or utilizing
25 an air-cooled conveyor or a conveyor which has a water-
26 chilled surface to cool the polymer strands or pellets.
27 However, these methods are more expensive and less efficient
28 than passing hot polymer in the form of strands, pellets, or
29 film through a water bath, and these methods require the
30 installation of new equipment in many existing commercial
31 ionomer production facilities. In addition, ionomer may
32 discolor when using these cooling means, since the ionomer

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1 rapidly oxidizes when it is maintained at elevated
2 temperatures for the extended periods of time inherent in
3 these other cooling means.

4 (1) Cooling ionomer in an aqueous acid bath

5 In a preferred embodiment, highly water-dispersible ionomer
6 of this invention may be cooled in an acid bath to prevent
7 dispersion of much of the ionomer. Highly water-dispersible
8 ionomer typically has a high sodium acrylate content which
9 makes the ionomer water-soluble. It is believed that ion
10 exchange occurs predominantly on the surface of the polymer
11 when passing hot ionomer strands through the acid bath,
12 replacing metal ions on the surface of the polymer with
13 hydrogen ions from the acid. It is believed that this makes
14 the surface of the strands or pellets acidic and
15 substantially reduces their water solubility.

16 Infrared analysis of ionomer pellets which were cooled in an
17 acid bath detected no acid groups. However, it is believed
18 that the concentration of acid groups in the overall ionomer
19 pellets was so small that it was undetectable by infrared
20 analysis of the bulk ionomer.

21 Almost any inorganic or water-soluble organic acid can be
22 used in the acid bath. A dilute aqueous solution of a non-
23 oxidizing acid is preferred to reduce processing cost and to
24 improve the washing efficiency when rinsing any excess acid
25 off of the polymer. The following list is illustrative of
26 the types of acids which may be used: sulfuric acid, formic
27 acid, propionic acid, oxalic acid, and the like. Preferred
28 acids are hydrochloric acid, phosphoric acid, and acetic
29 acid.

30 The temperature of the acid solution is preferably that
31 temperature which produces ionomer which has not discolored

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1 and which provides ionomer at the appropriate temperature
2 for any subsequent processing steps, such as drying. The
3 temperature of the acid solution is typically between about
4 5 to 50°C, and preferably is between about 10 and 30°C.

5 Example 16 illustrates this method for cooling ionomer using
6 an aqueous acid solution.

(2) Acidification of a clear copolymer of ethylene and esters and metal salts of alpha, beta-ethylenically-unsaturated carboxylic acids

11 In one embodiment, compositions of this invention have
12 carboxylic acid groups, in which case the compositions can
13 be represented as copolymers comprising comonomers of alpha-
14 olefins, esters of alpha, beta-ethylenically-unsaturated
15 carboxylic acids, metal salts of alpha, beta-ethylenically-
16 unsaturated carboxylic acids, and alpha, beta-ethylenically-
17 unsaturated carboxylic acids. Acid groups can plasticize
18 the composition and increase its melt index. This permits
19 tailoring of polymer properties such as polymer flow
20 viscosity, tear strength, polymer reactivity with food, and
21 odor or taste for a particular application.

22 Acidification of a composition comprising a copolymer of
23 alpha-olefins, esters of alpha, beta-ethylenically-
24 unsaturated carboxylic acids, and metal salts of alpha,
25 beta-ethylenically-unsaturated carboxylic acids can occur in
26 a reaction section of a reactive extruder. Preferably,
27 acidification occurs in a second reaction section when using
28 reactive extrusion, and preferably after the composition
29 comprising the reaction product of a copolymer of alpha-
30 olefins and esters of alpha, beta-ethylenically-unsaturated
31 carboxylic acids has been saponified with a Group IA metal-
32 containing solution in a first reaction section.

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1 Other equipment may be used in place of a reactive extruder
2 for acidification of a saponified composition. For example,
3 a Brabender Plasticorder, a resin kettle, or an autoclave
4 may be used.

5 A non-oxidizing acid can be used at a temperature and in a
6 concentration which does not cause significant degradation
7 of the copolymer or composition. Typically, the amount of
8 acid required is the amount which provides the desired
9 weight percent of acid groups per combined weight of acid
10 and copolymer to be acidified. Examples of these acids
11 include phosphoric acid, hydrochloric acid, benzoic acid,
12 lactic acid, and stearic acid. Polymeric non-oxidizing
13 acids can also be used, such as ethylene-acrylic acid
14 copolymer, exemplified by Dow Chemical Company's Primacor
15 Grade 3330. The non-oxidizing acids may have only one or
16 two monomer units, such as benzoic acid or acetic acid, or
17 they may comprise polymeric acids having multiple monomer
18 units and having a molecular weight well in excess of one
19 million, such as Primacor Grade 3330. Phosphoric acid,
20 lactic acid, and polymer acids are preferred. Typical
21 temperatures for acidification are between about 190 and
22 300°C, and preferably are between about 230 and 300°C. The
23 acid concentration is preferably between 10 and 95%.

24 In certain applications or compositions of this invention,
25 any byproducts of acidification can remain in the
26 composition. For other applications or compositions, any
27 byproducts of acidification and/or any excess acid can be
28 removed from the ionomer by washing with water or other
29 solvent and filtering the composition. For example, polymer
30 acidified using phosphoric acid can be washed with water in
31 an autoclave. The byproduct salt in the aqueous phase can
32 subsequently be separated from the polymer by filtration.

- 31 -

1 (3) Acidification of hazy non-acidic ionomer to
2 improve clarity

3 Acid can also be used to improve the clarity of an ionomer
4 which has high haze and little or no acid functionality
5 present before acidification. This provides an easy and
6 inexpensive means for rendering these opaque polymers less
7 hazy or even clear. In a preferred embodiment, the adhesion
8 of the acidified polymer improves as well. In another
9 preferred embodiment, the melt index of the ionomer also
10 increases.

11 The ionomer to be acidified has a haze greater than 10% but
12 otherwise has the same chemical analysis of components as
13 described in the preceding section for adding acid functions
14 to a clear but non-acidic ionomer composition of this
15 invention. Acidification is also preferably performed as
16 described in the preceding section. Uniform mixing of the
17 acid and ionomer, as supplied by a reactive extruder, for
18 example, provides a consistent and clearer acidified
19 ionomer. In the examples, the haze of the ionomer to be
20 acidified exceeded 90% and could be reduced in half and even
21 by 75%.

22 The previous section also specifies the types of acids
23 useful for acidifying hazy ionomers. The amount of acid
24 required for acidification is that amount which provides an
25 ionomer film having at most half of the haze that was
26 present in the non-acidified ionomer. The amount of acid
27 used also should not exceed that amount which is necessary
28 to provide the greatest reduction in haze for the particular
29 ionomer and acid used. As Tables 22 and 23 show, haze
30 begins to increase again once the amount of acid is
31 increased beyond the amount necessary to provide minimum
32 haze for the particular ionomer and acid. Therefore, excess

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1 acid beyond the amount required to reduce the haze to its
2 minimum value is to be avoided.

3 When the acidified ionomer is analyzed, as little as 0.05
4 mole of acidic monomer need be present in the ionomer per
5 mole of the saponified monomer that was originally present
6 in the ionomer prior to acidification. For example, when
7 ethylene-methyl acrylate-sodium acrylate ionomer having
8 greater than 10% haze is made from ethylene-methyl acrylate
9 copolymer having 20 weight percent methyl acrylate which is
10 25% hydrolyzed using aqueous sodium hydroxide, the ionomer
11 has approximately 5.4 weight percent sodium acrylate, or
12 about 1.9 mole percent sodium acrylate. Acidification of at
13 least 5% of the sodium acrylate groups decreases the haze of
14 this ionomer. Preferably, the amount of acidic monomer in
15 the acidified ionomer is greater than 0.07 mole per mole of
16 hydrolyzed monomer present in the non-acidified ionomer, and
17 preferably the amount of acidified ionomer is greater than
18 0.1 mole per mole. Examples 20-23 illustrate this method of
19 making clearer ionomers from hazy ionomers.

20 D) Uses of the compositions

21 Ionomer compositions of this invention can be formed into
22 single or multi-layer films using conventional equipment.
23 For example, cast, extruded, or blown film can be made.

24 An ionomer composition of this invention can be coextruded
25 with or laminated to other polymers such as nylon
26 (unoriented and oriented), polyester (unoriented and
27 oriented), polystyrene, vinyl acetate, polyacrylonitrile,
28 polyvinylidene dichloride, and polyolefins such as
29 polypropylene (unoriented and oriented), polyethylene (low
30 density, high density, and linear low density), ethylene-
31 methyl (meth)acrylate copolymers, ethylene-ethyl
32 (meth)acrylate copolymers, ethylene-(meth)acrylic acid
33 copolymers, ethylene-vinyl alcohol copolymers, ethylene

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1 vinyl acetate copolymers, and other polymers and their
2 derivatives capable of being coextruded. Typical uses for
3 ionomer compositions of this invention include their use in
4 single-layer or multi-layer films, where they can be used as
5 tie layers or used for imparting flexibility, strength, hot
6 tack, and/or heat seal capabilities. Such uses include
7 stretch films, bundling (shrink) wrap, food and drug
8 packaging, and skin packaging for protecting the contents of
9 a package.

10 Single-layer ionomer film or multi-layer film in which the
11 ionomer is on one face of the film can be used as a surface
12 protection layer for products such as glass, polycarbonate
13 or poly(methyl methacrylate) products, which can be used in
14 windshields for vehicles or windows. The ionomer layer
15 protects products from scratches and/or nicks because of the
16 ionomer's abrasion resistance. The ionomer's adhesion to
17 such substrates is excellent, yet it can be peeled readily
18 from the surface. The transparency of the ionomer of this
19 invention allows visual inspection of the surface of the
20 wrapped product, permitting a customer to inspect a product
21 for flaws prior to receipt and unwrapping of the product.

22 Single-layer ionomer film or multi-layer film containing
23 ionomer of this invention can be used to make easy-open
24 packaging such as easy-tear film, bags, pouches and parcels.
25 A tear propagates linearly through the film, and the
26 Elmendorf tear strength of the ionomer indicates that it is
27 well-suited to uses such as easy-opening packaging. The
28 package in which the film is incorporated normally is
29 notched or incorporates a tear strip to facilitate ease of
30 opening of the package.

31 The ionomer of this invention can also serve as its own tie
32 layer due to its good adhesion to other layers. This

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1 eliminates the need for separate tie layers in a multi-layer
2 film, reducing the thickness of the multi-layer film and
3 reducing the overall cost of making the multi-layer film.

4 Ionomer compositions of this invention may also be used in
5 thermally extruded and thermally formed products such as
6 automotive interior parts and skin packaging. The ionomer
7 compositions may be used alone or in combination with other
8 polymers in blow-molded or injection molded articles,
9 particular where such articles need to be grease- and oil-
10 resistant such as bottles for fragrances or detergents, and
11 the compositions may also be used in articles such as food
12 trays formed by vacuum thermo-forming. The ionomer
13 compositions of this invention may be used in making
14 articles such as golf ball covers; coated fabrics;
15 orthopedic, prosthetic and medical devices; recreational
16 equipment; and footwear components. The ionomer
17 compositions of this invention are especially useful in
18 applications where the ionomer properties discussed above,
19 as well as the excellent abrasion resistance, transparency,
20 and/or directional tear properties of the ionomer, are
21 useful.

22 Theories discussed herein are intended to provide possible
23 explanations for what was observed. These theories are not
24 to be interpreted as limiting the invention described
25 herein. Also, the following examples are illustrative and
26 are not intended to limit the invention disclosed herein.

27 EXAMPLE 1

28 An ethylene-methyl acrylate copolymer (manufactured by
29 Chevron by the method disclosed in U.S. Patent
30 No. 3,350,372) containing 20% by weight methyl acrylate
31 (7.5 mole %) and having a melt index of 400 g/10 min.
32 (190°C) was fed to a Werner & Pfleiderer corrosion-resistant

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1 ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. The
2 extruder had a ratio of length to diameter of about 44. The
3 screw configuration for Examples 1-13 and Comparative
4 Example A is given in Table 1 column A. Aqueous sodium
5 hydroxide (50% NaOH by weight in all examples, except where
6 noted otherwise) was fed to Zone 3 of the extruder at
7 9.3 lbs./hr. The screw speed was 550 rpm.

The following extruder temperatures were measured:

Table 2

| | | | | | | | | |
|----|-------------|-----|-----|-----|-----|-----|-----|-----|
| 10 | Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 11 | Temperature | 236 | 350 | 253 | 253 | 230 | 245 | 260 |
| 12 | (°C) | | | | | | | |

13 Note: Zone 1: melting section for polymer to be reacted;
14 Zone 2 & 3: reaction section;
15 Zone 4: devolatilization section;
16 Zones 5-7: extrusion section.

17 Water from the sodium hydroxide solution and the reaction
18 by-product methanol were removed by a two-stage
19 devolatilization. In all examples, the evolved water and
20 methanol from the first devolatilization stage were
21 condensed at atmospheric pressure. The second
22 devolatilization stage was connected to a vacuum system in
23 all examples. The second devolatilization stage had 28.4
24 in. Hg vacuum during this run.

25 The reaction product was extruded through an eight-strand
26 die, cooled on a stainless steel belt (about 20 feet in
27 length, made by Sandvik) which was chilled by cold water
28 underneath the belt, and subsequently pelletized.

29 The product had a melt flow rate of 0.33 g/10 min. (230°C).
30 The product had a hydrolysis of 53% (i.e., 53% of the methyl

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1 acrylate in the ethylene-methyl acrylate copolymer was
2 converted to sodium acrylate).

3 The polymer was made into blown film on a Victor blown film
4 line at the following processing conditions:

5 **Table 3**

| 6 Zone 1 | 7 Zone 2 | Zone 3 | Adapter | Die 1 | Die 2 | Die Pressure | Melt Temperature |
|----------|----------|--------|---------|-------|-------|--------------|------------------|
| 7 400°F | 440°F | 515°F | 435°F | 430°F | 440°F | 7600 psi | 440°F |

8 The blown film had a thickness of 3.5 mils. The haze of the
9 film was 2%, and the 60° gloss was 122. The 1% secant
10 moduli of the film were 12,740 and 10,080 psi respectively
11 for the machine direction (MD) and the transverse direction
12 (TD).

13 All haze values were measured using the method of
14 ASTM D 1003. The 60° gloss values were measured using the
15 method of ASTM D 2457. The 1% secant modulus values and
16 tensile strength values were measured using the method of
17 ASTM D-638.

18 Melt index of feed resin was measured by the method of
19 ASTM D 1239, using a temperature of 190°C and a 2.16 kg
20 weight. The melt flow rate of a composition of this
21 invention was determined by the method of ASTM D 1239 but
22 using a temperature of 230°C rather than 190°C and using a
23 2.16 kg weight.

24 The hydrolysis of the product is defined as the moles of
25 metal salt of the alpha, beta-ethylenically-unsaturated
26 carboxylic acid present in the product, expressed as a
27 percentage of the moles of the ester of alpha,
28 beta-ethylenically-unsaturated carboxylic acid present prior

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1 to saponifying the copolymer. The terms "hydrolysis",
2 "extent of hydrolysis", "percent hydrolysis", "percent
3 saponified", and "extent of saponification" are used
4 interchangeably.

5 The extent of hydrolysis is determined by dissolving 10 g.
6 of ionomer in 250 ml. of tetrahydrofuran (THF) in a 500 ml.
7 round-bottom flask, to which 1 ml. of glacial acetic acid is
8 added. The flask is fitted with a refluxing condenser, and
9 the contents are boiled for about 20 min. The mixture is
10 poured into 1 liter of cold distilled water (about 15-20°C),
11 and then filtered. The precipitate is subsequently washed
12 with about 3 liters of distilled water. The precipitate is
13 dried under vacuum, then weighed and dissolved in THF and
14 titrated with 0.1 N potassium hydroxide in ethanol, using
15 thymol blue to indicate the end-point of titration. The
16 extent of hydrolysis is then calculated by dividing the
17 moles of potassium used in titrating the sample by the moles
18 of ester present in the initial ethylene-methyl acrylate
19 copolymer prior to the saponification reaction.

EXAMPLE 2

20 The ethylene-methyl acrylate copolymer of Example 1 was fed
21 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin
22 screw extruder at a rate of 100 lbs./hr. Aqueous sodium
23 hydroxide was fed to Zone 3 of the extruder at a rate of
24 11.2 lbs./hr. The screw speed was 500 rpm.
25

26 The following temperatures were measured during the process:

27 Table 4

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 271 | 252 | 255 | 256 | 230 | 231 | 241 |

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1 The vacuum on the second devolatilization zone was 28.4 in.
2 Hg. The reaction product was extruded, cooled on a Sandvik
3 belt and pelletized in the same way as Example 1. The
4 product had a melt flow rate of 0.20 g/10 min. (230°C). The
5 hydrolysis of the product was 65%.

6 The polymer was made into blown film on a Victor blown film
7 line using the processing conditions similar to those in
8 Example 1. The haze of the blown film was 2%, and the 60°
9 gloss was 133. The film had a tensile strength of 4010 and
10 3180 psi respectively for MD and TD. The 1% secant moduli
11 of the film were 14720 and 13110 psi respectively for MD and
12 TD.

EXAMPLE 3

14 The ethylene-methyl acrylate copolymer of Example 1 was fed
15 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin
16 screw extruder at a rate of 100 lbs./hr. Aqueous sodium
17 hydroxide was fed to Zone 3 on the extruder at a rate of
18 12.1 lbs./hr. The screw speed was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 5

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 218 | 347 | 255 | 255 | 230 | 251 | 260 |

24 The vacuum on the second devolatilization zone was 28.5 in.
25 Hg. The reaction product was extruded, cooled on a Sandvik
26 belt and pelletized in the same way as Example 1. The
27 product had a melt flow rate of 0.1 g/10 min. (230°C). The
28 hydrolysis of the product was 70%.

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1 The polymer was made into blown film on a Victor blown film
2 line using the processing conditions similar to those in
3 Example 1. The haze of the blown film was 2%, and the 60°
4 gloss was 134. The film had a tensile strength of 4470 and
5 2420 psi respectively for MD and TD.

6 EXAMPLE 4

7 An ethylene-methyl acrylate copolymer containing 20% by
8 weight methyl acrylate and having a melt index of
9 570 g/10 min. (190°C) was fed to the Werner & Pfleiderer
10 corrosion-resistant ZSK-40mm twin screw extruder at a rate
11 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
12 on the extruder at a rate of 13.0 lbs./hr. The screw speed
13 was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 6

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 178 | 242 | 254 | 252 | 301 | 303 | 289 |

19 The vacuum on the second devolatilization zone was 25.5 in.
20 Hg. The reaction product was extruded, cooled on a Sandvik
21 belt and pelletized in the same way as Example 1. The
22 product had a melt flow rate of 0.87 g/10 min. (230°C). The
23 hydrolysis of the product was 69%.

24 The polymer was made into blown film on a Victor blown film
25 line using the processing conditions similar to those in
26 Example 1. The haze of the blown film was 2%, and the 60°
27 gloss (ASTM D 2457) was 135. The film had a tensile
28 strength of 2870 and 1760 psi respectively for MD and TD.

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EXAMPLE 5

1 An ethylene-methyl acrylate copolymer containing 20% by
2 weight methyl acrylate and having a melt index of
3 440 g/10 min. (190°C) was fed to the Werner & Pfleiderer
4 corrosion-resistant ZSK-40mm twin screw extruder at a rate
5 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
6 on the extruder at a rate of 13.0 lbs./hr. The screw speed
7 was 500 rpm.

9 The following temperatures were measured during the process:

10

Table 7

11

12

13

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 189 | 257 | 257 | 258 | 251 | 263 | 283 |

14

The vacuum on the second devolatilization zone was 28.4 in.
15 Hg. The reaction product was extruded, cooled on a Sandvik
16 belt and pelletized in the same way as Example 1. The
17 product had a melt flow rate of 0.81 g/10 min. (230°C). The
18 hydrolysis of the product was 72%.

19

The polymer was made into blown film on a Victor blown film
20 line using the processing conditions similar to those in
21 Example 1. The haze of the blown film was 2%, and the 60°
22 gloss was 135. The film had a tensile strength of 2600 and
23 1850 psi respectively for MD and TD.

24

EXAMPLE 6

25 An ethylene-methyl acrylate copolymer containing 23% by
26 weight methyl acrylate and having a melt index of
27 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
28 corrosion-resistant ZSK-40mm twin screw extruder at a rate
29 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

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1 on the extruder at a rate of 10.7 lbs./hr. The screw speed
2 was 500 rpm.

3 The following temperatures were measured during the process:

4 **Table 8**

| 5 Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|
| 6 Temperature (°C) | 181 | 247 | 256 | 255 | 255 | 254 | 270 |

8 The vacuum on the second devolatilization zone was 26.7 in.
9 Hg. The reaction product was extruded, cooled on a Sandvik
10 belt and pelletized in the same way as Example 1. The
11 product had a melt flow rate of 0.54 g/10 min. (230°C). The
12 hydrolysis of the product was 51%.

13 The polymer was made into blown film on a Victor blown film
14 line using the processing conditions similar to those in
15 Example 1. The haze of the blown film was 2%, and the 60°
16 gloss was 124. The film had a tensile strength of 2270 and
17 1470 psi respectively for MD and TD.

18 **EXAMPLE 7**

19 An ethylene-methyl acrylate copolymer containing 23% by
20 weight methyl acrylate and having a melt index of
21 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
24 on the extruder at a rate of 12.8 lbs./hr. The screw speed
25 was 500 rpm.

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1 The following temperatures were measured during the process:

2

Table 9

3

4

5

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 175 | 247 | 253 | 259 | 254 | 257 | 271 |

6 The vacuum on the second devolatilization zone was 26.6 in.
 7 Hg. The reaction product was extruded, cooled on a Sandvik
 8 belt and pelletized in the same way as Example 1. The
 9 product had a melt flow rate of 0.45 g/10 min. (230°C). The
 10 hydrolysis of the product was 61%.

11 The polymer was made into blown film on a Victor blown film
 12 line using the processing conditions similar to those in
 13 Example 1. The haze of the blown film was 3%, and the 60°
 14 gloss was 132. The film had a tensile strength of 2730 and
 15 1960 psi respectively for MD and TD.

16

EXAMPLE 8

17 An ethylene-methyl acrylate copolymer containing 23% by
 18 weight methyl acrylate and having a melt index of
 19 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
 20 corrosion-resistant ZSK-40mm twin screw extruder at a rate
 21 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
 22 on the extruder at a rate of 9.6 lbs./hr. The screw speed
 23 was 500 rpm.

24

The following temperatures were measured during the process:

25

Table 10

26

27

28

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 193 | 284 | 257 | 259 | 254 | 254 | 271 |

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1 The vacuum on the second devolatilization zone was 26.2 in.
2 Hg. The reaction product was extruded, cooled on a Sandvik
3 belt and pelletized in the same way as Example 1. The
4 product had a melt flow rate of 0.60 g/10 min. (230°C). The
5 hydrolysis of the product was 46%.

6 The polymer was made into blown film on a Victor blown film
7 line using the processing conditions similar to those in
8 Example 1. The haze of the blown film was 2%, and the 60°
9 gloss was 120. The film had a tensile strength of 1950 and
10 1240 psi respectively for MD and TD.

11 EXAMPLE 9

12 An ethylene-methyl acrylate copolymer containing 22% by
13 weight methyl acrylate and having a melt index of
14 470 g/10 min. (190°C) was fed to the Werner & Pfleiderer
15 corrosion-resistant ZSK-40mm twin screw extruder at a rate
16 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
17 on the extruder at a rate of 14.3 lbs./hr. The screw speed
18 was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 11

| 21 Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|-----|-----|-----|-----|-----|-----|-----|
| 22 23 Temperature (°C) | 298 | 326 | 255 | 266 | 254 | 254 | 271 |

24 The vacuum on the second devolatilization zone was 28.4 in.
25 Hg. The reaction product was extruded, cooled on a Sandvik
26 belt and pelletized in the same way as Example 1. The
27 product had a melt flow rate of 0.23 g/10 min. (230°C). The
28 hydrolysis of the product was 70%.

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1 The polymer was made into blown film on a Victor blown film
2 line using the processing conditions similar to those in
3 Example 1. The haze of the blown film was 1%, and the 60°
4 gloss was 134. The film had a tensile strength of 3000 and
5 2170 psi respectively for MD and TD.

6 EXAMPLE 10

7 An ethylene-methyl acrylate copolymer containing 23% by
8 weight methyl acrylate and having a melt index of
9 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
10 corrosion-resistant ZSK-40mm twin screw extruder at a rate
11 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
12 on the extruder at a rate of 8.6 lbs./hr. The screw speed
13 was 500 rpm.

14 The following temperatures were measured during the process:

15

Table 12

16
17
18

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 177 | 262 | 255 | 253 | 254 | 255 | 270 |

19 The vacuum on the second devolatilization zone was 25.8 in.
20 Hg. The reaction product was extruded, cooled on a Sandvik
21 belt and pelletized in the same way as Example 1. The
22 product had a melt flow rate of 1.25 g/10 min. (230°C). The
23 hydrolysis of the product was 41%.

24 The polymer was made into blown film on a Victor blown film
25 line using the processing conditions similar to those in
26 Example 1. The haze of the blown film was 4%, and the 60°
27 gloss was 104. The film had a tensile strength of 1910 and
28 970 psi respectively for MD and TD.

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EXAMPLE 11

1 An ethylene-methyl acrylate copolymer containing 20% by
2 weight methyl acrylate and having a melt index of
3 100 g/10 min. (190°C) was fed to the Werner & Pfleiderer
4 corrosion-resistant ZSK-40mm twin screw extruder at a rate
5 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
6 on the extruder at a rate of 4.7 lbs./hr. The screw speed
7 was 500 rpm.

9 The following temperatures were measured during the process:

10 Table 13

| 11 Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|-----|-----|-----|-----|-----|-----|-----|
| 12 Temperature (°C) | 253 | 322 | 254 | 230 | 230 | 231 | 241 |

14 The vacuum on the second devolatilization zone was 28.4 in.
15 Hg. The reaction product was extruded, cooled on a Sandvik
16 belt and pelletized in the same way as Example 1. The
17 product had a melt flow rate of 0.67 g/10 min. (230°C). The
18 hydrolysis of the product was 26%.

19 The polymer was made into blown film on a Victor blown film
20 line using the processing conditions similar to those in
21 Example 1. The haze of the blown film was 3%, and the 60°
22 gloss was 115. The film had a tensile strength of 1150 and
23 1080 psi respectively for MD and TD.

EXAMPLE 12

24 An ethylene-methyl acrylate copolymer containing 20% by
25 weight methyl acrylate and having a melt index of
26 400 g/10 min. (190°C) was fed to the Werner & Pfleiderer
27 corrosion-resistant ZSK-40mm twin screw extruder at a rate
28 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

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1 on the extruder at a rate of 9.3 lbs./hr. The screw speed
2 was 500 rpm.

3 The following temperatures were measured during the process:

4 Table 14

| 5 Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|
| 6 Temperature 7 (°C) | 209 | 201 | 266 | 255 | 256 | 256 | 256 |

8 The vacuum on the second devolatilization zone was 24.7 in.
9 Hg. The reaction product was extruded, cooled in a water
10 bath, and pelletized. The pellets were dried in a vacuum
11 over at 65°C and 29.5 in. Hg for 48 hours. The product had
12 a melt flow rate of 0.66 g/10 min. (230°C). The hydrolysis
13 of the product was 49%.

14 The polymer was made into blown film on a Victor blown film
15 line using the processing conditions similar to those in
16 Example 1. The haze of the blown film was 3%, and the 60°
17 gloss was 128.

18 EXAMPLE 13

19 An ethylene-methyl acrylate copolymer containing 20% by
20 weight methyl acrylate and having a melt index of
21 150 g/10 min. (190°C) was fed to the Werner & Pfleiderer
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
24 on the extruder at a rate of 7.4 lbs./hr. The screw speed
25 was 450 rpm.

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1 The following temperatures were measured during the process:

2

Table 15

3

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 188 | 199 | 276 | 253 | 257 | 260 | 262 |

4

5

6 The vacuum on the second devolatilization zone was 28.5 in.
7 Hg. The reaction product was extruded, cooled in a water
8 bath, and pelletized. The pellets were dried in a vacuum
9 over at 65°C and 29.5 in. Hg for 48 hours. The product had
10 a melt flow rate of 0.22 g/10 min. (230°C). The hydrolysis
11 of the product was 42%.

12 The polymer was made into blown film on a Victor blown film
13 line using the processing conditions similar to those in
14 Example 1. The haze of the blown film was 4%, and the 60°
15 gloss was 122.

16

EXAMPLE 14

17 An ethylene-methyl acrylate copolymer containing 20% by
18 weight methyl acrylate and having a melt index of
19 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer
20 ZSK-58mm twin screw extruder at a rate of 425 lbs./hr. The
21 screw was configured to provide substantially the same
22 mixing as provided in the ZSK-40mm extruder in Examples 1-
23 13. Aqueous sodium hydroxide was fed to the reaction zone
24 on the extruder at a rate of 56 lbs./hr.

25

26

27

28

The screw speed of the extruder was at 500 rpm. The
temperatures in the reaction zones were 226°C to 338°C. The
product was 71% hydrolyzed. The product had similar optical
properties to the product of Example 3.

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1

EXAMPLE 15

2

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer ZSK-70mm twin screw extruder at a rate of 450 lbs./hr. The screw was configured to provide substantially the same mixing as provided in the ZSK-40mm extruder in Examples 1-13. Aqueous sodium hydroxide was fed to the reaction zone on the extruder at a rate of 50 lbs./hr.

10

The screw speed of the extruder was at 580 rpm. The temperatures in the reaction zones were 330°C to 350°C. The product was 61% hydrolyzed. The product had similar optical properties to the product of Example 3.

14

COMPARATIVE EXAMPLE A

15

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 20 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 4.6 lbs./hr. The screw speed was 400 rpm.

22

The following temperatures were measured during the process:

23

Table 16

24

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 216 | 213 | 270 | 269 | 270 | 271 | 270 |

25

26

27

The vacuum on the second devolatilization zone was 27.9 in. Hg. The reaction product was extruded, cooled in a water bath, and pelletized. The pellets were dried in a vacuum over at 65°C and 29.5 in. Hg for 48 hours. The product had

- 49 -

1 a melt flow rate of 3.2 g/10 min. (190°C). The hydrolysis
2 of the product was 15%.

3 The polymer was made into blown film on a Victor blown film
4 line using the processing conditions similar to those in
5 Example 1. The haze of the blown film was 81%, and the 60°
6 gloss was 35.

7 This Comparative Example A shows that saponifying 15% of the
8 methyl acrylate groups to form the sodium salt of acrylic
9 acid is insufficient at these reaction conditions to produce
10 the low haze of compositions of this invention.

COMPARATIVE EXAMPLE B

11 An ethylene-methyl acrylate copolymer containing 20% methyl
12 acrylate by weight and having a melt index of 400 g/10 min.
13 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant
14 extruder at 13.2 lbs/hr. 1.73 lbs/hr. of 35% sodium
15 hydroxide solution was fed to zone 3 of the extruder. The
16 extruder had the configuration of elements shown in Table 1
17 column B.

19 The following extruder temperatures were measured:

20

Table 17

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 230 | 275 | 275 | 275 | 275 | 240 | 235 |

24 Water and the by-product methanol were removed in a two-
25 stage devolatilization zone. The polymer strands were
26 cooled in a water bath and pelletized. The pellets were
27 vacuum-dried overnight at about 25 in. Hg vacuum and at
28 68°C.

- 50 -

1 Chemical analysis of the product indicated a degree of
2 saponification of 49.2%. The product had a melt index
3 (190°C) of 0.54 g/10 min.

4 A 1/2 inch Randcastle miniextruder was used to make a cast
5 film of about 4 inch width. The temperature at the feed
6 zone and barrels 1A through 3A was 430°C, while the die
7 temperature was 440°C. The film had a haze of 55% and a 60°
8 gloss of 20.

9 It is believed that the poor clarity of this example results
10 from a more dilute caustic solution and poorer mixing at
11 these reaction conditions as compared to the conditions
12 which produce compositions of this invention.

13 COMPARATIVE EXAMPLE C
14 An ethylene-methyl acrylate copolymer containing 20% methyl
15 acrylate by weight and having a melt index of 400 g/10 min.
16 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant
17 extruder at 13.2 lbs/hr. 2.29 lbs/hr. of 35% sodium
18 hydroxide solution was fed to zone 3 of the extruder. The
19 extruder had the configuration of elements shown in Table 1
20 column B.

21 The following extruder temperatures were measured:

22 Table 18

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 230 | 275 | 275 | 275 | 275 | 240 | 235 |

26 Water and the by-product methanol were removed in a two-
27 stage devolatilization zone. The polymer strands were
28 cooled in a water bath and pelletized. The pellets were

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1 vacuum-dried overnight at about 25 in. Hg vacuum and at
2 68°C.

3 Chemical analysis of the product indicated a degree of
4 saponification of 65.2%. The product had a melt flow rate
5 of 0.38 g/10 min. (230°C).

6 A 1/2 inch Randcastle miniextruder was used to make a cast
7 film of about 4 inch width. The temperature at the feed
8 zone and barrels 1A through 3A was 430°C, while the die
9 temperature was 440°C. The film had a haze of 15% and a 60°
10 gloss of 66.

11 This comparative example shows that a greater extent of
12 hydrolysis provided clearer ionomer, but mixing conditions
13 as supplied by the screw design of Table 1 column B when
14 using 35% aqueous caustic did not appear to provide the
15 intensive mixing and reaction conditions necessary to obtain
16 a haze of 10% or less.

COMPARATIVE EXAMPLE D

17 Ethylene-methyl acrylate copolymer having 20 weight percent
18 methyl acrylate and a 400 melt index (190°C) was saponified
19 with a 35% by weight aqueous solution of sodium hydroxide
20 per the method of Comparative Example B. The product was
21 60% saponified and had a melt index (190°C) of 0.06. The
22 tensile strength in the machine direction was 1582 psi.
23

COMPARATIVE EXAMPLE E

24 Ethylene-methyl acrylate copolymer having 25 weight percent
25 methyl acrylate and a 457 melt index (190°C) was saponified
26 with a 35% by weight aqueous solution of sodium hydroxide
27 per the method of Comparative Example B. The product was
28 44% saponified and had a melt index (190°C) of 0.04. The
29 tensile strength in the machine direction was 985 psi.
30

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EXAMPLE 16 -- ACID BATH COOLING OF IONOMER

26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of Example 1 were fed to a Werner & Pfleiderer corrosion resistant ZSK-30 twin-screw extruder having the configuration of elements given in Table 1 column C. 50% aqueous sodium hydroxide was fed into zone 3 at 2.5 lb./hr. The screw speed was 500 rpm.

The following extruder temperatures were measured:

Table 19

| Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) | 174 | 200 | 255 | 260 | 254 | 267 | 255 |

Volatile components were removed in a two port devolatilization section, and the second port had a vacuum of 28 in. Hg. The polymer strands from a four-strand die were cooled in a 5% phosphoric acid bath which was 10 ft. long, and were then rinsed in a 2 ft. water bath and pelletized in a Conair pelletizer.

During 1.75 hours of operation, the ionomer was efficiently cooled and pelletized, and the acid bath remained acidic and clear with no evidence of dissolved polymer. Total carbon analysis of the cooling water (determined by potentiometric titration) at the end of operation showed less than 20 ppm of dissolved carbon. By contrast, when the same polymer was cooled in water, the water bath became turbid and milky-white within a few minutes of operation.

The resulting pellets were colorless, shiny, and clear.

28

EXAMPLE 17

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1 This example shows a copolymer of ethylene, methyl acrylate,
2 sodium acrylate, and acrylic acid. First, ethylene-methyl
3 acrylate copolymer having 20 weight percent methyl acrylate
4 and 153 melt index (190°C) was saponified in a Werner-
5 Pfleiderer ZSK-30 twin-screw reactive extruder using 50%
6 aqueous sodium hydroxide and substantially the same reaction
7 conditions as Example 16. The extent of saponification was
8 42%. The pelletized ionomer was clear and glossy and had a
9 melt flow rate (230°C) of 0.17 g/10 min.

10 The ionomer pellets were fed to the extruder at a rate of 12
11 kg/hr. 85.6% aqueous phosphoric acid was fed to Zone 3 of
12 the extruder at a rate of 0.14 kg/hr., and the product was
13 extruded, cooled in a water bath, and pelletized.

14 The product retained its clear and glossy optical
15 properties, and the melt flow rate increased to 1.0 g/10
16 min. (230°C). Film that was made on the Randcastle mini-
17 extruder had a tensile strength in the machine direction of
18 2418 psi.

EXAMPLE 18

19 Ethylene-methyl acrylate copolymer having 20 weight percent
20 methyl acrylate and 400 melt index (190°C) was saponified in
21 a ZSK-30 extruder having the configuration of elements given
22 in Table 1 column C with 50% aqueous sodium hydroxide at a
23 reaction temperature of about 148°C. The screw speed was
24 500 rpm. The copolymer was fed to the extruder at a rate of
25 12 kg/hr., and the product was about 54% saponified. The
26 product was visually clear.

COMPARATIVE EXAMPLE F

28 Ethylene-methyl acrylate copolymer having 20 weight percent
29 methyl acrylate and 400 melt index (190°C) was saponified
30 with 50% aqueous sodium hydroxide in a ZSK-30 extruder

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1 having the configuration of screw elements given in Table 1
2 column B at a reaction temperature of about 149°C. The
3 screw speed was 500 rpm. The copolymer was fed to the
4 extruder at a rate of 16 kg/hr., and the product was about
5 52% saponified. The product was visually cloudy.

6 This example shows that insufficient mixing was supplied by
7 the screw configuration of Table 1 column B at these
8 reaction conditions.

EXAMPLE 19

26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of Example 1 were fed to a Werner & Pfleiderer corrosion resistant ZSK-30 twin-screw extruder having the configuration of elements given in Table 1 column C. 50% aqueous potassium hydroxide was fed into zone 3 at the rate given in Table 20. The screw speed was 500 rpm.

16 The extruder temperatures were substantially the same as
17 those given in Table 19. Volatile components were removed
18 in a two port devolatilization section, and the second port
19 had a vacuum of 28 in. Hg. The following table summarizes
20 the feed rate of potassium hydroxide, the melt flow rate
21 (230°C), and the extent of saponification of the methyl
22 acrylate groups.

TABLE 20

| Feed rate (lb./hr.) of 50% aqueous potassium hydroxide | Melt flow rate of ionomer of this Example | Extent of saponification |
|---|---|-----------------------------|
| 1.87 | 1.66 | 27 |
| 2.62 | 0.60 | 37 |
| 3.74 | 0.23 | 53 |
| 5.28 | 0.07 | 78 |

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COMPARATIVE EXAMPLE G

1 An ethylene-methyl acrylate copolymer containing 20% methyl
2 acrylate by weight and having a melt index of 20 g/10 min.
3 (190°C) was fed to a Werner & Pfleiderer ZSK-40 corrosion-
4 resistant extruder at 100 lbs/hr. 4.7 lbs/hr. of 50% sodium
5 hydroxide solution was fed to zone 3 of the extruder. The
6 screw speed was 275 rpm.
7

8 The following extruder temperatures were measured:

9 Table 21

| 10 Zone No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|-----|-----|-----|-----|-----|-----|-----|
| 11 Temperature (°C) | 200 | 208 | 279 | 280 | 278 | 280 | 281 |

12 The vacuum on the second devolatilization zone was 27.0 in.
13 Hg. The reaction product was extruded, cooled in a water
14 bath, and pelletized. The pellets were dried in a vacuum
15 over at 65°C and 29.5 in. Hg for 48 hours. The product had
16 a melt index of 1.6 g/10 min. (190°C). The hydrolysis of
17 the product was 24%.

18 The polymer was made into blown film on a Victor blown film
19 line using the processing conditions similar to those in
20 Example 1. The haze of the blown film was 97%, and the 60°
21 gloss was 43.

22 The SEM micrograph shown in Figure 2 was taken on a freeze-
23 fractured surface of the blown film made from this ionomer.

EXAMPLE 20

24 Ethylene-methyl acrylate copolymer having 20% by weight
25 methyl acrylate and a melt index of 20 g/10 min. (190°C) was
26 hydrolyzed by the method of Comparative Example A, and
27 25% hydrolyzed by the method of Comparative Example A, and
28

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1 this sodium ionomer was ground to 60 mesh-sized powder. 10
2 grams of the ground ionomer were put into a 500 ml single-
3 neck round-bottom flask, and 250 ml of stabilized THF and a
4 magnetic stirrer were added. The above mixture was heated
5 to reflux and stirred for about 10 minutes to ensure that
6 the ionomer dissolved. After dissolution, 1.6 ml of 2 N
7 aqueous hydrochloric acid was added to the flask. The
8 reaction continued for 2 hours, then the solution was
9 precipitated in 1 liter of cold water, filtered, and dried
10 under vacuum.

11 The reaction produced 9.7 grams of white polymer precipitate
12 having a melt index of 0.9 g/10 min. (190°C). Fourier-
13 transform infrared (FT-IR) analysis showed that the
14 carboxylic acid group was present (1708 cm⁻¹, absorbance
15 1.5259) as well as sodium acrylate (1558 cm⁻¹, absorbance
16 1.0294). This indicated that 60% of the sodium acrylate
17 groups present in the ionomer prior to acidification was
18 converted to acid groups, thus giving a stoichiometric
19 reaction of this acid with sodium acrylate. The acidified
20 ionomer was a tetrapolymer of ethylene, methyl acrylate,
21 sodium acrylate, and acrylic acid having about 5.7 mole
22 percent methyl acrylate, 0.8 mole percent sodium acrylate,
23 and 1.1 mole percent acrylic acid. The melt index of the
24 acidified ionomer was 6.3 g/10 min. (190°C).

25 The acidified ionomer had excellent adhesion to a polar
26 substrate such as unprimed aluminum foil. Both non-
27 acidified ionomer and acidified ionomer were separately
28 pressed between two pieces of unprimed aluminum foil in a
29 hydraulic press having two heated plates. The pellets and
30 foil were heated without pressure for about 5 minutes at
31 350°C, then the pressure was increased to 20,000 psi and
32 maintained for an additional 5 minutes at 350°C. The

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1 acidified ionomer sealed the aluminum foil and could not be
2 separated from it without tearing the foil. The non-
3 acidified ionomer was easily peeled from the foil.

4 Separate films of acidified ionomer and non-acidified
5 ionomer were each made by placing 0.2 g of the ionomer
6 between two pieces of Mylar film. The ionomer was heated
7 and pressed as above. The Mylar was separated from the
8 ionomer with a small amount of acetone. The acidified
9 ionomer film was clear, having no observable haze and having
10 an observable high gloss. The non-acidified ionomer film
11 was opaque, dull, and frosty.

EXAMPLE 21

12 Example 20 was repeated, except that 0.2556 g of glacial
13 acetic acid was substituted in place of the hydrochloric
14 acid. The reaction produced 9.8 grams of acidified ionomer
15 as a white precipitate. FT-IR analysis indicated that 80%
16 of the sodium acrylate present in the ionomer prior to
17 acidification were converted to acid groups. The acidified
18 ionomer was a tetrapolymer of ethylene, methyl acrylate,
19 sodium acrylate, and acrylic acid, having about 5.7 mole
20 percent methyl acrylate, 0.4 mole percent sodium acrylate,
21 and 1.5 mole percent acrylic acid in the acidified ionomer.
22 The acidified ionomer had a melt index of 11.7 g/10 min.
23 (190°C).

24 The acidified ionomer produced a clear film with no
25 observable haze and observably high gloss. The non-
26 acidified ionomer produced opaque, dull, and frosty film.
27 The acidified ionomer also exhibited excellent adhesion to
28 aluminum foil, particularly when compared to the non-
29 acidified ionomer.

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1 An ethylene-methyl acrylate copolymer having 20 weight
 2 percent methyl acrylate and a melt index of 153 g/10 min.
 3 (190°C) was 35% hydrolyzed by the method of Comparative
 4 Example A. The melt index of this ionomer was 9.7 g/10 min.
 5 (190°C), and the haze of a cast film was 98%, the 60° gloss
 6 was 6, and the tear strength (g/mil) in the machine
 7 direction was 33 and in the transverse direction was 41.

8 This ionomer was fed continuously at a rate of 10 kg/hr to
 9 the Werner-Pfleiderer ZSK-30 extruder which was maintained
 10 at 210°C. Primacor Grade 3330 was also fed continuously to
 11 the extruder in the ratio given below, and the properties of
 12 a cast film of the acidified copolymer made on the
 13 Randcastle mini-extruder are listed in Table 22.

14

Table 22

| 15 Kg. Primacor per Kg. Ionomer | 16 Melt index (g/10 min. @ 190°C) | 17 Haze (%) | 18 60° gloss | 19 Tear strength, g/mil, machine direction | 20 Tear strength g/mil, trans- verse direc- tion |
|---|--|-------------------|--------------------|---|---|
| 19 0.076 | 20 6.6 | 21 48 | 22 18 | 23 26 | 24 21 |
| 20 0.152 | 21 5.6 | 22 70 | 23 11 | 24 24 | 25 38 |
| 21 0.228 | 22 4.3 | 23 82 | 24 9 | 25 18 | 26 57 |

22

EXAMPLE 23

23 The non-acidified ionomer of Example 22 was fed continuously
 24 to the extruder at a rate of 8 kg/hr. and was acidified
 25 using 21.5% phosphoric acid, as detailed below. The
 26 properties of a cast film of the acidified copolymer made on
 27 the Randcastle mini-extruder are listed in Table 23.

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Table 23

| 1 | 2 | 3 | 4 | 5 | Kg H ₃ PO ₄ (21.5%) / kg. ionomer | Melt index (190°C) | Haze (%) | 60° gloss | Tear strength (g/mil), machine direction | Tear strength (g/mil), trans- verse direc- tion |
|---|--------|------|----|----|--|--------------------------|-------------|--------------|--|---|
| 6 | 0.0375 | 8.0 | 46 | 18 | 28 | 36 | | | | |
| 7 | 0.0738 | 20.0 | 23 | 51 | 45 | 43 | | | | |
| 8 | 0.1113 | 36.3 | 23 | 51 | 71 | 49 | | | | |
| 9 | 0.1488 | 57.3 | 32 | 35 | 79 | 70 | | | | |

10 Tear strength was measured using the method of ASTM D-1922.

11 EXAMPLE 24

12 An ethylene-methyl acrylate copolymer having 20 weight
13 percent methyl acrylate was saponified substantially by the
14 method of Example 1. The percent hydrolysis and properties
15 of the polymer are listed in the following Table 24.

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TABLE 24

| % HYDRO- LYZED | % HAZE | 60° GLOSS | TENSILE STRENGTH, psi | | 1° SECANT MODULUS, psi | | MELT POINT TEMP. °C | ELMENDORF TEAR STRENGTH, g/mil | ELONGA- TION @ BREAK, % |
|----------------------|-----------|--------------|-----------------------------|------|---------------------------|-------|------------------------------|---|----------------------------------|
| | | | MD | TD | MD | TD | | | |
| 35 | 13.3 | 55 | 1709 | 1445 | 7893 | 7667 | 77 | 12 | 14 |
| 42 | 1.4 | 126 | 2081 | 1928 | 14831 | 14054 | 76 | 17 | 24 |
| 50 | 0.5 | 140 | 2321 | 1984 | 8193 | 7718 | 73 | 26 | 22 |
| | | | | | | | | 365 | 405 |

Melt point temperature was measured using a differential scanning calorimeter and standard methods well-known in the art.

Elmendorf tear strength was measured using ASTM D-1922.

Elongation at break was measured using ASTM D-882.

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1 The hot tack strength for these ionomers is summarized in
 2 Figure 3.

EXAMPLE 25

3 Samples of ethylene methyl acrylate copolymer having the
 4 methyl acrylate contents in following Table 25 were
 5 saponified to various degrees of hydrolysis using
 6 substantially the method of Example 1. In addition,
 7 ethylene methyl acrylate copolymers made by the method of
 8 U.S. Ser. No. 07/947,870, filed Sep. 21, 1992, where all of
 9 the methyl acrylate was fed to a first reaction zone of a
 10 multi-zone high-pressure polymerization reactor, were
 11 saponified to various degrees of hydrolysis. Table 25
 12 summarizes the melt point temperatures of these ionomers.
 13

14

Table 25

| 15 16 17 | WT. % METHYL ACRYLATE | ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. 3,350,372 | | ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. SER. NO. 07/947,870 | |
|----------------|-----------------------------|--|-------------------------|--|-------------------------|
| | | % HYDROLYZED | MELT POINT TEMP., °C | % HYDROLYZED | MELT POINT TEMP., °C |
| 18 | 12. | 62 | 90 | 60 | 97 |
| 19 | 12 | 86 | 83 | 83 | 99 |
| 20 | 12 | -- | -- | 83 | 98 |
| 21 | 12 | 100 | 87 | 99 | 93 |
| 22 | 20 | -- | -- | 35 | 92 |
| 23 | 20 | 47 | 87 | 42 | 91 |
| 24 | 20 | 51 | 86 | 50 | 91 |
| 25 | 20 | 61 | 83 | 65 | 92 |
| 26 | 20 | 72 | 64 | -- | -- |
| 27 | 24 | 42 | 64 | -- | -- |

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EXAMPLE 26

1 Ionomer was made substantially by the method of Example 1.
2 This ionomer was cast coextruded individually with three
3 polymers on a Randcastle Mini-Extruder to form three 2-layer
4 films, where each layer was 2 mil thick. Adhesion strength
5 of the 2-layer films was analyzed using TAPPI Uniform Method
6 541, "Adhesion to Non-Porous Flexible Substrates", which is
7 incorporated by reference in its entirety herein.
8 Ionomer/propylene film (Fina 3275) had an adhesion of 770
9 g/inch; ionomer/high density polyethylene (Chevron HiD®
10 9650) could not be separated; and ionomer/nylon (Allied
11 Chemical's Capron 8350) had an adhesion of 80 g/inch.
12

13 The heat seal strength of the ionomer/polyethylene film
14 above is summarized in Figure 4.

EXAMPLE 27

15 Ethylene-methyl acrylate-butyl acrylate copolymer containing
16 10 weight percent methyl acrylate and 10 weight percent
17 butyl acrylate is about 50% hydrolyzed substantially by the
18 method of Example 1. This yields an ethylene-methyl
19 acrylate-butyl acrylate-sodium acrylate copolymer. It is
20 expected that the methyl acrylate reacts at a faster rate
21 than the butyl acrylate, so more methyl acrylate is
22 converted to the sodium salt than butyl acrylate. This
23 product is useful in applications where a higher melt-point
24 temperature is desired, such as films or bags which contact
25 hot food or liquids.
26

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1 WE CLAIM:

2 1. A method of making an ionomer composition comprising:

3 A) contacting:

4 (1) a Group IA metal-containing solution with

5 (2) a molten or fluid copolymer comprising alpha-

6 olefins having from two to eight carbon atoms

7 and esters of alpha, beta-ethylenically-

8 unsaturated carboxylic acids having from four

9 to twenty two carbon atoms and having a melt

10 index between about 100 and about 2000 g/10

11 min., as measured by ASTM method D 1239 at

12 190°C; and

13 B) intensively mixing the copolymer and Group IA

14 metal-containing solution at a temperature and to

15 an extent which provides an ionomer composition

16 having no more than ten percent haze.

17 2. The method of claim 1 wherein the copolymer comprises

18 ethylene methyl acrylate copolymer.

19 3. The method of claim 1 or 2 wherein said copolymer has a

20 melt index between 300 and 600 g/10 min.

21 4. The method of any of claims 1-3 wherein the Group IA

22 metal-containing solution comprises aqueous metal

23 hydroxide, where the metal is selected from the group

24 consisting of sodium and potassium.

25 5. The method of claim 4 wherein the concentration of

26 metal hydroxide in the aqueous metal hydroxide is at

27 least 50 percent by weight.

28 6. The method of any of claims 1-5 wherein the intensive

29 mixing is provided by a twin-screw extruder.

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- 1 7. The method of any of claims 1-6 wherein the intensive
2 mixing occurs at a temperature between 200 and 350°C.
- 3 8. The method of claim 7 wherein the temperature is
4 between 275 and 350°C.
- 5 9. The method of any of claims 1-8 wherein the intensive
6 mixing provides an ionomer composition substantially
7 free of ionic clusters greater than 0.05 micron in
8 size.
- 9 10. A composition made by the method of any of claims 1-9.
- 10 11. A composition comprising a copolymer of alpha-olefins
11 having from two to eight carbon atoms, esters of alpha,
12 beta-ethylenically-unsaturated carboxylic acids having
13 from four to twenty-two carbon atoms, and metal salts
14 of acrylic or methacrylic acid, wherein said copolymer
15 has a haze of no more than ten percent as measured by
16 ASTM method D 1003.
- 17 12. The composition of claim 10 or 11 having a haze of no
18 more than seven percent.
- 19 13. The composition of claim 12 having a haze of no more
20 than five percent.
- 21 14. The composition of claim 13 having a haze of no more
22 than two percent.
- 23 15. The composition of any of claims 10-14 wherein the
24 alpha-olefin consists essentially of ethylene.

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- 1 16. The composition of any of claims 10-15 wherein the
2 metal of said metal salt is selected from the group
3 consisting of sodium, lithium, and potassium.
- 4 17. The composition of any of claims 10-16 wherein said
5 ester comprises methyl acrylate.
- 6 18. The composition of any of claims 10-17 wherein the
7 metal of said metal salt consists essentially of
8 sodium.
- 9 19. The composition of any of claims 10-18 wherein said
10 metal salt of acrylic or methacrylic acid comprises
11 between about 1.9 and about 7.5 mole percent of said
12 copolymer.
- 13 20. The composition of any of claims 10-19 wherein said
14 esters of alpha, beta-ethylenically-unsaturated
15 carboxylic acid comprise between about 2.3 and about
16 7.4 mole percent of said copolymer.
- 17 21. The composition of any of claims 10-20 wherein said
18 alkali metal salt of alpha, beta-ethylenically-
19 unsaturated carboxylic acid comprises between about 3.0
20 and about 6.5 mole percent of said copolymer.
- 21 22. The composition of any of claims 10-21 wherein said
22 esters of alpha, beta-ethylenically-unsaturated
23 carboxylic acid comprise between about 2.8 and about
24 6.3 mole percent of said copolymer.
- 25 23. The composition of any of claims 10-22 wherein the
26 composition is acidified.

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1 chosen from the group consisting of phosphoric acid,
2 hydrochloric acid, and acetic acid.

3 35. A method for reducing the haze of a copolymer
4 comprising combining:
5 A) acid; and
6 B) a copolymer of alpha-olefins having from two to
7 eight carbon atoms, esters of alpha, beta-
8 ethylenically-unsaturated carboxylic acids having
9 from four to twenty-two carbon atoms, and metal
10 salts of acrylic or methacrylic acid, wherein said
11 copolymer has a haze of greater than ten percent
12 as measured by ASTM method D 1003
13 and uniformly mixing the copolymer and acid in an
14 amount and at conditions sufficient to reduce the haze
15 of a film.

16 36. A method for reducing the haze and increasing the melt
17 index of a copolymer comprising combining:
18 A) acid; and
19 B) a copolymer of alpha-olefins having from two to
20 eight carbon atoms, esters of alpha, beta-
21 ethylenically-unsaturated carboxylic acids having
22 from four to twenty-two carbon atoms, and metal
23 salts of acrylic or methacrylic acid, wherein said
24 copolymer has a haze of greater than ten percent
25 as measured by ASTM method D 1003
26 and uniformly mixing the copolymer and acid in an
27 amount and at conditions sufficient to reduce the haze
28 of a pressed film.

29 37. A method for reducing the haze and increasing the
30 adhesion of a copolymer comprising combining:
31 A) acid; and

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1 B) a copolymer of alpha-olefins having from two to
2 eight carbon atoms, esters of alpha, beta-
3 ethylenically-unsaturated carboxylic acids having
4 from four to twenty-two carbon atoms, and metal
5 salts of acrylic or methacrylic acid, wherein said
6 copolymer has a haze of greater than ten percent
7 as measured by ASTM method D 1003
8 and uniformly mixing the copolymer and acid in an
9 amount and at conditions sufficient to reduce the haze
10 of a pressed film.

11 38. The method of any of claims 35-37 wherein the copolymer
12 and acid are mixed in an extruder.

13 39. The method of any of claims 35-37 wherein the copolymer
14 is dispersed in solvent and acidified.

15 40. The method of any of claims 35-39 wherein the acidified
16 copolymer has a haze of no more than ten percent as
17 measured by ASTM method D 1003.

18 41. The method of any of claims 35-40 wherein the alpha-
19 olefin consists essentially of ethylene.

20 42. The method of any of claims 35-41 wherein metal of said
21 metal salt is selected from the group consisting of
22 sodium, lithium, and potassium.

23 43. The method of any of claims 35-42 wherein said ester
24 comprises methyl acrylate.

25 44. The method of any of claims 35-43 wherein the metal of
26 said metal salt consists essentially of sodium.

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- 1 45. The method of any of claims 35-44 wherein said metal
2 salt of acrylic or methacrylic acid comprises between
3 about 1.9 and about 7.5 mole percent of said copolymer.
- 4 46. The method of any of claims 35-45 wherein said esters
5 of alpha, beta-ethylenically-unsaturated carboxylic
6 acid comprise between about 2.3 and about 7.4 mole
7 percent of said copolymer.
- 8 47. The method of any of claims 35-46 wherein said alkali
9 metal salt of alpha, beta-ethylenically-unsaturated
10 carboxylic acid comprises between about 3.0 and about
11 6.5 mole percent of said copolymer.
- 12 48. The method of any of claims 35-47 wherein said esters
13 of alpha, beta-ethylenically-unsaturated carboxylic
14 acid comprise between about 2.8 and about 6.3 mole
15 percent of said copolymer.
- 16 49. The method of any of claims 35-48 wherein the acid is a
17 polymeric acid.
- 18 50. The method of any of claims 35-48 wherein the acid is
19 phosphoric acid.

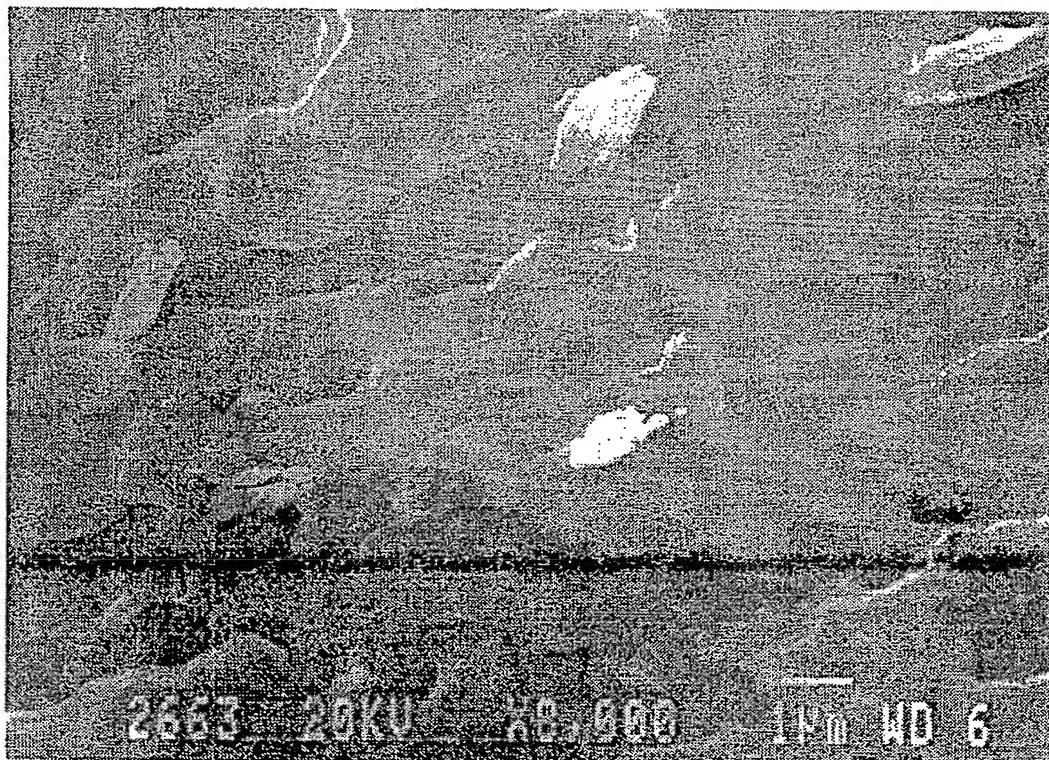


FIGURE 1

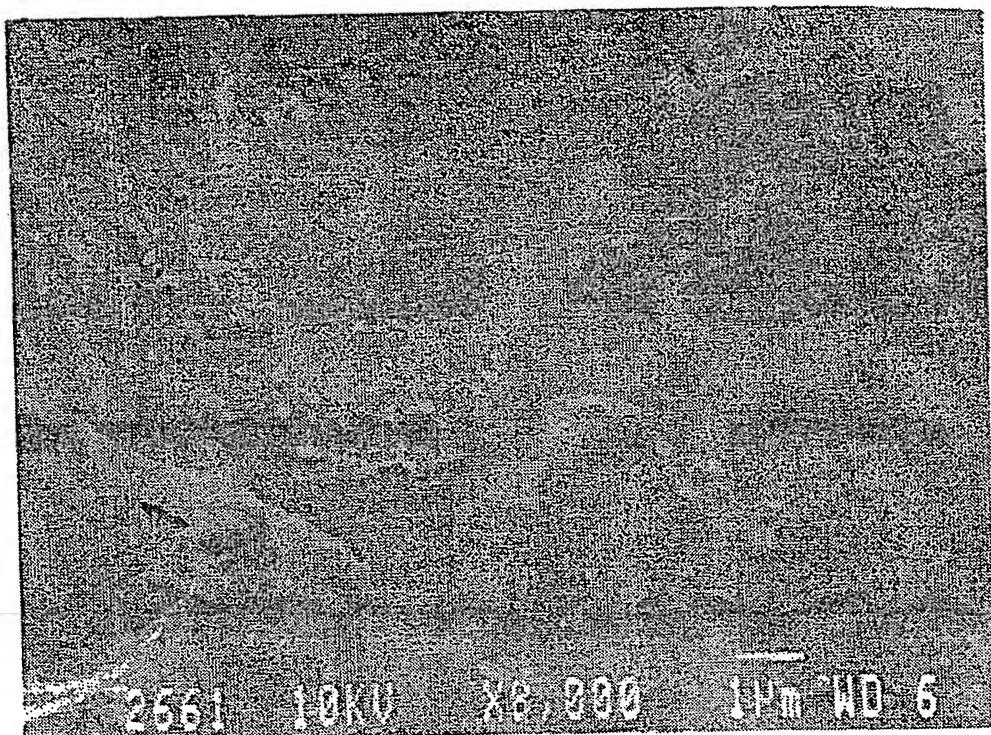


FIGURE 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/12366

A. CLASSIFICATION OF SUBJECT MATTER

C 08 F 8/00, C 08 J 5/18, // (C 08 F 210/02,
C 08 F 220:06)

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 F, C 08 J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|---|
| A | EP, A, 0 194 677 (NIPPON PETROCHEMICALS CO LTD.) 17 September 1986 (17.09.86), claims 1,2,5-7,10; examples. -- | 1-8, 10, 15-22 |
| A | US, A, 5 218 057 (KURKOV et al.) 08 June 1993 (08.06.93), claims 1-15; examples 1-3; column 5, lines 3-9 (cited in the application). -- | 1,2, 4-8, 10,11, 15-23, 25 |
| A | GB, A, 1 011 981 (E.I.DU PONT DE NEMOURS AND COMPANY) 01 December 1965 (01.12.65), claims 1,2,8-12,15; page 12, lines 50-54; page 10, | 1,2,4, 5,10, 11, 15-18, 27,29 |

Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

-2-

International application No.
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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|----------|---|--|
| A | product No.24. -- US, A, 3 264 272 (REES) 02 August 1966 (02.08.66), claims 1,3,4,7,8,18,20,30,33 (cited in the application). -- | 1,4,5, 10, 15-17, 27,29 |
| A | US, A, 3 970 626 (HURST et al.) 20 July 1976 (20.07.76), claims 1,3,4; example 1 (cited in the application). -- | 1,2, 4,5, 8-11, 15-22, 27,28 |
| A | US, A, 4 638 034 (Mc CLAIN) 20 January 1987 (20.01.87), claims 1-3,5-7 (cited in the application). -- | 1,2,4, 7,10, 15-23 |
| A | EP, A, 0 115 190 (E.I.DU PONT DE NEMOURS AND COMPANY) 08 August 1984 (08.08.84), page 10, comparative examples 1,3. -- | 1,3,4, 6-8, 10,15, 16,18 |
| A | US, A, 4 307 211 (ITO et al.) 22 December 1981 (22.12.81), claim 1. ----- | 1,7,8, 10,15 |

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

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|---|---|--|--|
| EP A2 194677 | 17-09-86 | DE CO 3689007 DE T2 3689007 EP A3 194677 EP B1 194677 JP A2 61209205 | 21-10-93 05-05-94 05-04-89 15-09-93 17-09-86 |
| US A 5218057 | 08-06-93 | EP A1 548352 EP A4 548352 FI A 930936 FI A0 930936 JP T2 6501519 NO A 930651 NO A0 930651 WO A1 9301219 | 30-06-93 29-12-93 03-03-93 03-03-93 17-02-94 24-02-93 24-02-93 21-01-93 |
| GB A 1011981 | | keine - none - rien | |
| US A 3264272 | | keine - none - rien | |
| US A 3970626 | 20-07-76 | BE A 692973 DE A1 1520778 SE B 317194 US A 3876452 NL A 6406361 | 03-07-67 08-02-73 10-11-69 08-04-75 07-12-64 |
| US A 4638034 | 20-01-87 | keine - none - rien | |
| EP A2 115190 | 08-08-84 | BR A 8307134 CA A1 1213389 DE CO 3373909 DK A0 6002/83 DK A 6002/83 DK B 167025 DK C 167025 EP A3 115190 EP B1 115190 JP A2 59133217 JP B4 5002687 KR B1 9102467 NO A 834816 NO B 164032 NO C 164032 US A 4690981 US A 4801649 ZA A 8309624 | 07-08-84 28-10-86 05-11-87 27-12-83 29-06-84 16-08-93 03-01-94 27-12-84 30-09-87 31-07-84 13-01-93 23-04-91 29-06-84 14-05-90 22-08-90 01-09-87 31-01-89 28-08-85 |
| US A 4307211 | 22-12-81 | keine - none - rien | |

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